The Pennsylvania State College Bulletin
Mineral Industries Experiment Station
Bulletin 14

PROCEEDINGS

of the Third

Pennsylvania Mineral Industries Conference

Ceramics Section

In Cooperation With

THE PITTSBURGH SECTION

of

THE AMERICAN CERAMIC SOCIETY

Held at

The Pennsylvania State College

October 20 and 21, 1933

FOREWORD

THE Pennsylvania Ceramic Conference held at the School of Mineral Industries on October 20 and 21, 1933, was the first technical ceramic conference ever held at the Pennsylvania State College. Organized, as it was, under the joint auspices of the School of Mineral Industries and the Pittsburgh Section of the American Ceramic Society, it gave an opportunity for practical technical men, executives and scientists to get together to discuss problems of mutual interest.

The main theme of the conference is the Heat Treatment of Ceramic Materials. Important structural changes occur in ceramic solids and glasses at high temperatures, and a knowledge of these alterations and the proper thermal treatment needed to bring them about, is one of the most fundamental problems in ceramics. The high quality of the papers presented is an indication of the thought and effort which ceramic leaders are devoting to this end.

The School of Mineral Industries is glad to welcome the industrial men at this conference, and to lay a foundation for real cooperation in solving the technical problems of one of Pennsylvania's greatest industries. Publication of the complete proceedings of such meetings makes a permanent record and provides bulletins for exchange purposes with libraries and educational institutions in this country and abroad.

NELSON W. TAYLOR,
Head, Department of Ceramics.

CONTENTS

CONTENTS (Continued)

ILLUSTRATIONS

ILLUSTRATIONS (Continued)

Change of Phase and Change of Constitution in the Solid State

By ROBERT B. SOSMAN

Research Laboratory, United States Steel Corporation, Kearny, N. J.

W HEN J. Willard Gibbs, as a result of purely mathematical and logical reasoning, announced in the year 1876[1] that there is a necessary numerical relation between the number of phases in a chemical system at equilibrium and the number of component substances necessary for the construction of that system, he drew a line that divided chemical phenomena sharply into two classes: phenomena of homogeneous equilibrium and phenomena of heterogeneous equilibrium. The differentiation was already familiar, it is true, but it was a qualitative differentiation only, of which no quantitative application had been made. Subsequent physico-chemical investigations have repeatedly proved the importance of the boundary then drawn, and even the rise of colloid chemistry does not seem likely to erase it.

Phases

A portion of matter is *homogeneous* when it is "uniform throughout, not only in chemical composition, but also in physical state."[2] A *phase* is a homogeneous portion of matter considered only with reference to its "composition and thermodynamic state." "All bodies which differ only in quantity and form [may be regarded] as different examples of the same phase."[3] The phase is the chemical unit on which Gibbs bases his mathematical reasoning, which, it may be remarked, embraces many other quantitative generalizations besides the familiar Phase Rule.

After remaining almost unnoticed for twenty years, Gibbs' generalization concerning phases was revived by van der Waals and elaborated by Roozeboom, and gradually built up into the complete doctrine that we now associate with the Phase Rule. Its deductions have been confirmed by thousands of experimental investigations, while chemists and physicists have been growing familiar with its logical derivation from the laws of thermodynamics. It has become an essential part of modern physical chemistry.

Leptons

Seventy years before Gibbs' discovery, John Dalton had announced an hypothesis whose later confirmation by all our chemical work has made it clear that there is no such thing as a strictly homogeneous phase. On the contrary, nothing is now more certain than that all matter

---

[1] Gibbs, J. Willard, "On the equilibrium of heterogeneous substances," Trans. Connecticut Acad. (1876) 3: 108-248; (1878) 3: 343-524. Collected Works (1928, New York) Vol. 1: 55-353.

[2] Gibbs, Coll. Works 1: p. 63.

[3] Ibid., p. 96.

consists of discrete but invisible atoms which are themselves highly complex in structure. The properties of a substance cannot possibly be the same from point to point; there is no such thing as "a mass uniform in chemical composition and in physical state."

Thus we have before us two sharply contrasted views of Nature, each of which fits a large body of experimental fact; yet they appear as mutually inconsistent as the wave theory and the quantum theory of radiation. I need hardly say to a scientific audience that it is idle to ask, which one of the two views is true? The best answer is to remind the inquirer that from a philosophical point of view the truth is never the same to two individuals, and that even the same individual never comprehends the same truth twice. In the present instance everything depends upon the keenness of vision with which the phenomena are viewed.

Thermodynamics is like life insurance; it is concerned only with the proved uniformities in the fate of great numbers of individuals, not with the variable fortunes of any one of them. So the thermodynamic chemist sees matter collected into phases with distinct boundaries, and finds by experiment that the smallest observable fragment or drop of such a phase contains so many millions of atoms, with such incomprehensible speeds and complexities of motion, that his utmost skill of eye and hand fails to disclose any difference in composition or properties between the right half and the left half of the fragment. It *is* homogeneous, so far as his available methods of testing are concerned.

The atomic chemist, on the other hand, and he may be the same individual, has ways of proving that the fragment is made up of very small but distinct leptons[4], including under this term protons, electrons, positrons, negatrons, neutrons, ions, atoms, atom-groups, and molecules. He can bombard the phase with high-speed particles ejected by a radioactive element, and actually see with the unaided eye the track left by a single particle as it bumps its way through the crowd; or he can recognize the turbidity caused by the fact that in any confused crowd there will momentarily be more densely packed knots and also spaces that are but sparsely occupied. He knows methods by which he can so finely subdivide the phase that the distinctly bounded particles contain only a few hundred atoms each, and can recognize phenomena arising from the fact that the skin or shell of such a particle may have properties different from those of its core or kernel.

It is this contrast between the two aspects of matter that I wish to emphasize in this address, bringing out the contrast in its particular bearing on certain problems of heterogeneous and homogeneous equilibrium.

Kinds of Homogeneous Phases

On the basis of their leptonic constitution and their mechanical properties several distinct types of homogeneous phases are recognized

[4] A useful term invented by F. Rinne: Das feinbauliche Wesen der Materie (1922, Berlin), p. 4; Crystals and the fine-structure of matter (London, 1924), p. 5.

in experimental studies of homogeneous and heterogeneous equilibrium. These types are classified in Table I*.

TABLE I.

Types of Homogeneous Phases

chaotic				crystalline	
expansive	condensed			condensed	
	fluid	resilient		resilient	fluid
Gas	Liquid	Glass		Crystal	Crystalline Liquid
		Solids			

The central theme announced for today's conference: ''Heat treatment in ceramics,'' indicates that our present consideration of phases must be confined to the two types which can be included under the designation of ''solid,'' namely: (1) resilient crystalline phases, (2) glassy phases.

The first step in a ''heat treatment'' is to raise the temperature of the object to be treated. Now, whether it had originally reached a steady state or not, it is almost a certainty that at the new temperature the system, especially if it consists of more than one component, will no longer be in a state of complete internal equilibrium. If the system is heterogeneous, reactions will begin at the boundaries between the grains, tending to establish new concentrations in the old phases, or even to establish wholly new phases, characteristic of the new temperature. With such reactions and their complexities we shall not attempt to deal, for every system has its own characteristic phases and concentrations whose interconnection cannot readily be generalized. Ignoring the boundary reactions, then, we shall confine our attention to the interior of an individual grain and see what changes it may undergo without any change of composition, just as if this grain alone were being heat-treated, or as if the object itself consisted of a single phase, such as a crystal of quartz or a porous lump of pure lime.

Polymorphism

The investigator trained in the application of the Phase Rule to chemical systems will ask at once concerning the phase selected for examination: Does this phase contain a polymorphous substance? If

---

* This classification is more fully discussed in an address on ''Crystals, solids, glasses, and liquids,'' to be given before the American Ceramic Society, Cincinnati meeting, February, 1934.

The possibility must not go unmentioned that there may exist phases in which some of the leptons are in a state of chaotic distribution and motion, while the rest of the leptons are in orderly crystalline arrangement.

it is polymorphous, he will ask further: What are the conditions of pressure and temperature under which each modification persists? For we know if there is but one component present, then at any arbitrarily selected temperature and pressure there can be but one stable phase consisting of this substance. The same is true even if there are two or more components, if the concentrations of the components in the phase are fixed.

In order to answer these unequivocal and practical questions, we proceed to examine the grain with all the different kinds of apparatus available in the physical laboratory, and we find that at the new temperature selected for heat treatment every one of its properties has changed measurably. In not a single respect is it exactly as it was at the original temperature. Is it still the same phase, or has the substance undergone a *change of phase?*

Confused Character of the Evidence on "Change of Phase"

The crystallographer, discovering three or four crystal faces or cleavage planes on the grain, and measuring their interfacial angles, reports: "There has been a change of axial ratio and a change of symmetry, but the change of symmetry is such that it could have been brought about by a small movement of certain atomic centers in one direction. By revising our idea of the original symmetry we can see that the change is not at all radical, and I believe we can say there has been no change of phase."

The X-ray physicist is then appealed to, and reports: "The Debye-Scherrer-Hull pattern obtained at the higher temperature is clearly different in spacing and in distribution of intensity from that obtained at low temperatures and I am sure that this is a new phase."

The optical physicist, when asked for his testimony, says: "The refractive indices are nearly the same numerically but the substance has changed from biaxial positive to biaxial negative in its birefringence. I think there has been a change of constitution, but not a change of phase."

The calorimetric expert then takes his turn, and announces: "There is a break in the heating and cooling curves of this substance, which is shown by more precise measurements to be due to a large and discontinuous change of heat capacity within a small range of temperature. This indicates that there has been an abrupt change of phase at the temperature of this anomaly."

In hope of obtaining some kind of decision, we refer the matter to the expert in thermal expansion, who announces: "The coefficients of expansion from room temperature are not abnormally large and are just what might be expected from a purely physical change. There has been no change of phase and no change of constitution."

Which one of the experts is right in his conclusion? Or are they all saying the same thing but using different words, so that the apparent disagreement is not real?

What is Polymorphism?

It would be easy at this point to become involved in argument over definitions, an entertaining pastime, one that has filled many pages of the journals, more by indirection than by design, but an occupation that is futile for scientific results. This is not to say that we should not have precise definitions of our terms, for precise definitions are very necessary in our phonetic and all too labile language. But we should be able to agree on our definitions and proceed quickly to the facts.

There is general agreement that the term "polymorphism" shall be confined to crystalline substances. When liquid and glassy, as well as crystalline, states are included, the term "allotropy" is used.[5] The dictionary and text-book definitions, however, are unsatisfactory, because they refer vaguely to "fundamental forms" or "distinct forms" without describing specifically something that can be observed or measured in the laboratory. The following is offered as covering all the generally recognized cases of polymorphism:

> That quality of a crystalline substance which permits it to appear in modifications belonging to different classes of symmetry, or differing in axial ratio or in specific volume to a degree not explainable by ordinary thermal dilatation or elastic compressibility.

For example: (1) Diamond and graphite are polymorphous forms of carbon because they belong to different classes of symmetry among the 32 classes recognized by crystallographers. (2) Rutile and anatase are polymorphous forms of titania, TiO_2, even though both forms crystallize with the symmetry of the ditetragonal-bipyramidal class, because they differ markedly in axial ratio. (3) α-iron and γ-iron are polymorphous forms of iron, even though they belong to the same symmetry-class and, being isometric, have necessarily the same axial ratio, because the metal undergoes a sudden change of specific volume at the inversion-temperature.

Compressibility is included in the definition along with thermal dilatation because pressure is a variable exactly analogous to temperature in its effect on properties; there are melting-pressures and inversion-pressures at constant temperature, just as there are melting-points and inversion-points at constant pressure.

We may next ask: Are there any changes of phase in the crystalline state that are not polymorphous changes? And conversely: Are there any polymorphous changes that are not changes of phase?

To answer these questions it is necessary to go back to Gibbs' original concept of a phase, and its place in the thermodynamic scheme. It is evident at once that the existence of critical points,—such as invariant-points, transition-points, melting-points,—is an essential part

---

[5] The term "allotropy" is sometimes defined as applicable only to the chemical elements, but the broader definition is justified both by the original usage (1850) and by current usage.

of the idea. Two or more phases must be conceived of as being in contact and capable of changing, the one into the other, by infinitesimal amounts as energy is added or subtracted, or as the temperature or the pressure is changed by a small amount.

Types of Polymorphism

Some allotropic and polymorphous changes can be observed to correspond well with the thermodynamic concept outlined above. The melting of ice in contact with water at 0°, and the transformation of quartz into tridymite at 870°, can be seen to be gradual transformations, proceeding from the boundary between the two phases, or proceeding by the initiation and growth of new nuclei, strictly controlled by the temperature and pressure and the supply of energy.

But there are many other polymorphous changes that come under the definition of polymorphism given above, yet do not correspond so well with the Phase-Rule picture. A well-known example is the alpha-beta or high-low[6] inversion of quartz. No gradual growth of the one modification at the expense of the other is observed in this and similar inversions. The transformation sweeps almost instantaneously through an entire crystal.

As will appear later, this type may justifiably be compared with a mechanical system such as a row of dominoes set on end. When the end block is upset the impulse is transmitted through the whole row and they all go down. There is never any equilibrium between standing and fallen blocks; they are either all up or all down. The row of dominoes is a system to which the thermodynamic reasoning used for phase equilibria does not apply. Nevertheless the effect of pressure on the inversion-temperature can be calculated by means of the thermodynamic formula, as Gibson[7] has shown for quartz and as Bridgman[8] has shown for the ammonium halides.

There are still other inversions that are like this high-low inversion of quartz in being reversible and discontinuous with respect to certain properties, yet are not polymorphous inversions under the definition. Such an inversion is the Curie point of pure iron, at which iron changes, with rising temperature, from the ferromagnetic to the paramagnetic state. There is no change of symmetry, of axial ratio, or of dimensions. There is, however, a discontinuous change of heat capacity and an easily measurable change of dilatation-coefficient[9] accompanying the very radical change in magnetic properties.

Using metaphorically certain aspects of the construction, alteration,

---

[6] Because of the confusion and difference of usage that has arisen in the application of the designations α and β, it is proposed to use the terms "high" and "low" for the high-temperature and low-temperature modifications, respectively. Journ. Franklin Inst. (1922) 194; p. 745.

[7] Gibson, R. E., Journ. Physical Chem. (1928) 32: 1197–1205.

[8] Bridgman, P. W., Physical Rev. (1931) 38: 182–191.

[9] Esser, H., & Müller, G. Arch. Eisenhüttenwesen (1933) 7: 265–268.

and decoration of a house, I propose for the moment to term these three types of change *reconstructive, alterative, and concealed.*[10]

1. Reconstructive polymorphism. Quartz-tridymite. The house is pulled down but the same bricks and lumber are used to rebuild it according to a new plan.

2. Alterative polymorphism. High-quartz and low-quartz. The frame of the house is undisturbed but the lighter partitions are pulled out and replaced according to a revised plan.

3. Concealed inversion. Ferromagnetic (α) and paramagnetic (β) iron. The plan of the house remains unaltered but it is rewired and redecorated.

The Structural Criterion for the Recognition of Phases

When the Phase Rule doctrine of heterogeneous equilibrium was first developed, it was the fashion to consider all of the inversions mentioned above,—reconstructive, alterative, and concealed—as ''changes of phase'' in a uniform sense. For example, iron at ordinary temperatures was designated α-iron. At 768°, the Curie point, it changed reversibly from the ferromagnetic state of α-iron to the paramagnetic state known as β-iron. β-iron, in turn, changed reversibly above 900° to γ-iron and γ-iron at 1400° to δ-iron. Roozeboom[11] himself had no hesitation in giving β-iron a place in the carbon-iron diagram as a distinct phase, of the same relative importance as α and γ. He was followed in this by Henry M. Howe and other distinguished investigators. It was known that there is a heat-effect at the α-β inversion, but very little information was available on changes in other properties.

At the moment, β-iron is a discredited phase, no longer shown distinct on the iron or the iron-carbon diagram. But it was not the consideration of the thermodynamic aspects of the inversion that brought β-iron into disrepute. It was principally the new insight into structure given by the X-rays, used according to the methods of Laue, Bragg, Debye, Scherrer, and Hull, that drove it out of the diagrams. The X-ray detects no perceptible change in the structure of α-iron at the α-β or Curie point. At the β-γ inversion, on the contrary, there is a clear change in structure from a body-centered to a face-centered lattice, while at the γ-δ point there is a sharp reversion to the body-centered lattice characteristic of α-iron.

As a consequence of this and similar discoveries, there has been a tendency to restrict the number of phases that are recognized as in good standing. The criterion has been tacitly set up that a phase of a polymorphous substance must have a distinct and unique space pattern of atoms in order to be recognized as different from another phase of the same substance. But if we ask what the space-lattice of atomic

---

[10] These terms are defined for the purposes of this address only, and are not offered for general use; a more thorough consideration and discussion of the subject of polymorphism would probably bring out better terms.

[11] Roozeboom, H. W. B., Zeitschr. physikal. Chemie (1900) 34: 437-487.

centers has to do with thermodynamic equilibrium the answer must be: Nothing at all. While it would not be fair to say that thermodynamics does not recognize the existence of leptons, it is certainly true that their mere arrangement in space is of no thermodynamic interest[12] unless this property can be connected up with the entropy and energy-content of masses of the substance that are large compared to a lepton.

A type of so-called polymorphism to which the Phase-Rule concept would certainly not apply, although the type might come under the definition in terms of symmetry, is that designated by Niggli[13] "architectonic polymorphism," and called by Groth and by Tutton[14] "polysymmetry." The merohedral (incomplete-faced) development of certain substances under special conditions of growth can be satisfactorily explained by the hypothesis that the elementary parallelepiped of one modification is only a constituent part of the elementary parallelepiped of the second modification. The one is in effect a polysynthetically though sub-microscopically twinned form of the other. Niggli suspects that orthoclase and microcline, also enstatite and clino-enstatite, may be examples of architectonic polymorphism. A phase-equilibrium between two modifications related in this way is hardly conceivable.

Other Interpretations of the Thermodynamic Criteria

The definition of what constitutes a crystalline phase, and the decision whether or not two given modifications of a substance, such as α- and β-iron, shall be treated as distinct phases, are evidently still a matter of arbitrary choice. Now Ehrenfest [15] has just come forward with proposals concerning methods of differentiating phases when these phases differ in new and unexpected ways. Keesom and his coworkers at Leiden[16] discovered last year a true discontinuity in the curve of heat capacity against temperature for liquid helium. Pressure causes a change in the temperature of the discontinuity, just as it changes the melting-point of ice or the inversion-point of rhombic and monoclinic sulfur. There is, then, no logical reason for refusing to recognize the P-T curve of this discontinuity as a true transition-curve between two *liquid phases of the same composition* but separated by no boundary, something hitherto unrecognized in the discipline of the Phase Rule.

The new and unfamiliar features of this situation are, first, the absence of any difference of specific volume, and, second, the absence of any difference of entropy, differences that have heretofore always been associated with a change of phase. Their relation to the thermody-

---

[12] "Molecular hypotheses * * * however admirable in themselves have no place in a thermodynamic argument." W. Lash Miller, Chem. Reviews (1925) 1: p. 295. But not all thermodynamicists will agree with this view.

[13] P. Niggli, Geometrische Kristallographie des Diskontinuums (1919, Leipzig) page 555.

[14] Tutton, Crystallography and practical crystal measurement (1922, London) p. 1263.

[15] Ehrenfest, P., "Phase-transformations in the customary and in the broader sense, classified according to the corresponding singularities of the thermodynamic potential," Proc. Sect. Sciences, Acad. Sci. Amsterdam (1933) 36: 153-157.

[16] Keesom. W. H., & Clusius, K., Proc. Acad. Sci. Amsterdam (1931) 34: 605; (1932) 35: 307, 736.

namic potential, however, makes it clear that we can extend the mathematical formulation and recognize "discontinuities of the second order" which are just as clearly definable as the "discontinuities of the first order" ordinarily recognized, though they may be more difficult to visualize in the form of a model of kinetic molecules. We must not be unduly prejudiced, however, by difficulties in securing acceptable models. Do not our ideas of what is "mathematical" and what is "real" rest upon nothing more secure than familiarity with the name and the concept? Entropy is no more a mathematical concept than is density or refractive index, when these ideas are resolved into their fundamentals.

To elucidate Ehrenfest's point of view: Entropy, which shows a first-order discontinuity in the familiar types of inversion, may be considered as the negative partial derivative of zeta (thermodynamic potential) with respect to temperature: $\dfrac{\delta Z}{\delta T} = -S$; specific volume, which also shows first-order discontinuities, is the partial derivative of zeta with respect to pressure: $\dfrac{\delta Z}{\delta p} = v$; in both cases it is assumed that zeta itself is continuous through the inversion point. Now assume that entropy and volume, instead of being discontinuous are, like zeta, continuous through a new kind of inversion-point. Then the second partial derivative of zeta with respect to temperature:

$$\frac{\delta^2 Z}{\delta T^2} = \frac{\delta S}{\delta T} = \frac{C_p}{T}$$

which is heat capacity (divided by temperature), becomes capable of having a discontinuity; and the second partial derivative of zeta with respect to pressure:

$$\frac{\delta^2 Z}{\delta p^2} = \frac{\delta v}{\delta p}$$

which is a compressibility, can also have a discontinuity; even though entropy and volume remain unchanged, as in the liquid helium investigated by Keesom.

Relations analogous to Clapeyron's equation can also be derived, and possess the merit of having already been proved experimentally in this very case.

Ehrenfest has not attempted to extend this principle in detail to discontinuities in other variables, such as magnetic susceptibility, but it evidently is capable of such extension.

Another interpretation of polymorphism from the purely thermo-dynamic point of view is that of Smits[17], who assumes that every poly-morphous substance contains at least two, and possibly more than two, molecular species which are spontaneously transformable into one an-other at greater or less speed. The substance must therefore be treated not as a one-component system but as a binary system. Although in-geniously worked out by Smits for a great variety of cases, the theory seems to be too purely formal in character to permit us to predict any facts about the polymorphism of a new and uninvestigated substance.[18]

Changes of Constitution

The preceding sections have been held as closely as possible to the thermodynamic point of view in their description of the various types of phases and phase-changes that may result from an altered tempera-ture. When we look more closely and admit the possibility of changes in the arrangement, configuration, and behavior of the unseen but real leptons, changes which we can assemble under the term "change of constitution," and which have already been touched upon in the dis-cussion of high- and low-quartz and α- and γ-iron, the opportunities to explain and also predict the behavior of matter under changing tem-perature are greatly enlarged.

This is not the place for any detailed description of atomic structures. While the physicists have now converted the atom into a highly atten-uated ethereal complex of quanta, eigenfunctions, and other mathe-matical images, the chemist need be in no haste to abandon his quite acceptable picture of the atom, showing a very small and heavy nucleus which consists of closely packed protons and nuclear electrons and con-tains nearly all the mass of the atom; at a considerable distance from this nucleus revolve the external electrons, like the planets of our Solar System, but in orbits which can have only certain fixed positions in accordance with the quantum principle of energy. This nucleus and solar system together constitute the atom. In solids, the electron orbits of neighboring atoms may interpenetrate, and it is this interpene-tration or electron-sharing that constitutes the principal type of bond-ing in the formation of chemical compounds and of crystals.

That the properties of the atom are of prime importance in determin-ing possibilities of polymorphism is plain from the thoroughgoing work of Goldschmidt and associates,[19] who worked out with the aid of X-rays the crystal structure of numerous interrelated series of inorganic sub-stances. The results show how the structure of a compound is de-termined by the characteristic radii of the constituent atoms and by their state of polarization.

The X-rays reveal only the regularities in the distribution of atomic nuclei. The orbital electrons go unperceived. Therefore, the most

[17] Smits, A., Theory of allotropy (1922, London).
[18] Properties of silica, p. 280.
[19] Goldschmidt, V. M., Barth, T., Lunde, G., & Zachariasen, W., Skr. Norske Vidensk. Akad. Oslo, 1926, No. 2.

obvious and most easily detected change of constitution within a homogeneous crystalline phase would be the shifting of arrangement of atomic nuclei which we might expect to be an essential part of a polymorphous inversion of the reconstructive type. X-ray studies of crystalline structure have given us abundant evidence that such a shifting of atomic centers does occur in this type of polymorphism.

The X-rays reveal a similar change of arrangement in polymorphous changes of the alterative type. Various physical properties, however, unite in indicating that there is some other kind of change which accompanies or precedes the change of structure. The effects of this other change begin to be noticeable at temperatures considerably removed from the inversion point, and become progressively greater as the inversion point is approached. Quartz, again, serves as a good example. Figure 1 demonstrates how the specific volume undergoes a progressively increasing change with rising temperature. The axial ratio, refractive index, rotatory power, electric conductivity,—in fact, all of the measured properties,—show this same effect.

The curve representing these changes is logarithmic in form.[20] Furthermore, it does not intersect the curve representing the same property for the high-temperature modification. Instead, there is a discontinuous change at the inversion point from the one curve to the other.

Another characteristic of the curves of some alterative inversions is the temperature-hysteresis. The temperature of the discontinuous change is lower when the temperature is falling, higher when the temperature is rising. This effect has been supposed by some investigators to be nothing more than a time lag, which would disappear if the heating and cooling were conducted slowly enough. Some color is given this view of the matter by small shiftings of the apparent inversion point that can actually be obtained by varying the rate, but there still remains a residual difference that can not be wiped out and seems independent of the time.[21]

This whole curve, with its four features of (1) logarithmically progressive approach, (2) discontinuity, (3) continuation on a wholly different curve, and (4) hysteresis on the return, has suggestive mechanical and electrical analogies. It duplicates the curve of angular velocity against the force exerted between two rotating concentric cylinders separated by a fluid; the discontinuity corresponds to the change from stream-line to turbulent motion in the fluid.[22] It also duplicates the curve of current against natural frequency in two coupled oscillatory electric c rcuits one of which is supplied by an electron tube.[23]

The picture suggested is that of moving mechanisms which mutually influence one another, and whose motion passes through a critical stage

[20] Wright, F. E., Journal Washington Acad. Sci. (1913) 3: 485-494.
[21] See also Dehlinger, U., Zeitschr. f. Physik (1932) 74: 267-290.
[22] Day, Sosman, & Hostetter, Amer. J. Sci. (1914) 37: p. 19.
[23] Sosman, J. Franklin Inst. (1922) 194: p. 757.

in changing discontinuously from one type of motion to another. I have based a theory of the high-low inversions of silica upon this parallelism.[24]

Subsequent studies of such inversions, particularly in metals, have shown that some polymorphous inversions do not consist of a single process but are made up of at least two stages. The progressively increasing and finally discontinuous change of symmetry in the alloy of composition AuCu, for example,[25] takes place as an independent action, which is then followed by that rearrangement of atomic centers which has been assumed by some investigators to constitute the whole of the process. A duality in such inversions was first suspected by Mügge,[26] who remarked on the apparent failure of synchronism between the change in birefringence and the change in shape and volume of quartz at the 573-degree inversion. Do the electron orbits shift independently of the nuclei?

It may be something of a strain on the imagination to picture a set of disembodied electron orbits temporarily divorced from their proper nuclei, yet we seem to have something of just this sort in the ferromagnetic modification of ferric oxide,[27] which retains the ferromagnetic properties of its parent magnetite, Fe_3O_4, although its own composition is Fe_2O_3.

Interpretation in Terms of Atomic Positions

In searching for the leptonic basis of the various phenomena of polymorphism, we can recognize that there are several variables relating entirely to the positions of atoms in a crystal, which might have an influence on the properties of the crystal. Such variables are: (1) the symmetry of the space-lattice of atomic positions; (2) the manner in which atoms are grouped around some selected atom taken as a center of reference (the coordination-number); (3) the distance between atomic centers; (4) the regularity of the distribution, where there are atoms or atom-groups of more than one kind; (5) the orientation of atoms with reference to symmetry-axes (which at present we have no means of testing); (6) the regularity of the orientation; (7) the position and orientation of atoms with reference to influences external to the crystal, such as an electromagnetic field.

Enough is already known about atomic positions to permit of a classification of inversion phenomena, such as that offered by Lange,[28] who, while admitting the close interconnection of different types of polymorphism, differentiates the following three kinds of phenomena as observed in metallic systems:

1. "Polymorphous inversion," characterized by a discontinuous change in the crystalline lattice,—either in the atomic spacing, the

[24] Properties of silica, p. 257.
[25] Dehlinger, V., & Graf, L., Zeitschr. f. Physik (1930) 64: 359–377.
[26] Mügge, O., Neues Jahrb. Min. etc. (1907) Festband: 181–196.
[27] Sosman, R. B., & Posnjak, E., Journ. Washington Acad. Sci. (1925) 15: 329–342.
[28] Lange, H., Zeitschr. technische Physik (1933) 14: 226–229.

atomic coordination-number, or the lattice symmetry. It occurs at a definite inversion-temperature.

2. "Hyperstructural inversion," characterized by a continuous change from an uncoordinated to a regularly coordinated state of the atoms.

3. "Magnetic inversion," characterized by some kind of continuous change within the atom or the crystal, not associated with any change in the dimensions or symmetry of the lattice.

It will be noted that Lange's use of the term "polymorphous" differs a litt e from the definition adopted on page 15. If we substitute, the word "structural" for "polymorphous" in his class 1, the nomenclature will remain consistent with that in the preceding portions of this paper.

Interpretation in Terms of Leptonic Movements

The formal possibilities are far from exhausted when we have considered the various possible positions of the nucleus. The atom and all its parts must be assumed to be in motion, and the amount and character of the motion should change with temperature.

One contrast in kinds of movement that has received particular attention is the contrast between oscillatory and rotational motion. Such a change would fit qualitatively the phenomena of an alterative inversion.[29]

What then are the oscillating or rotating units? If there are such things as electrons traveling in planetary orbits about the nucleus of each atom, and mutually influencing one another, they offer the very mechanism that we are looking for in order to explain the critical phenomena of alterative and magnetic inversions. But there is one problem that immediately presents itself: How can changing temperature affect the motions of such electrons? We are fairly sure now from the success of the electron theory of conduction in metals, as expounded by Lorentz and recently modified by Pauli, Sommerfeld, and others, that the electron energy in a metal is almost independent of temperature.

Nevertheless, temperature does have an effect on planetary electrons, and the evidence of this has come from an unexpected quarter,—the absorption spectra of solids. The usual absorption spectrum of a solid or liquid consists of a series of broad bands or lines with ill-defined edges, not good for much because not amenable to precise measurement. Freed and Spedding[30] predicted from ferromagnetic theories that certain rare-earth elements, particularly samarium and gadolinium, would have sharp spectral lines at low temperatures, and proved experimentally[31] that they do. A study of these lines yields the information that

[29] Properties of silica, (1927), p. 258.
[30] Physical Rev. (1929) 34: 945-953.
[31] Freed, S., Journ. Amer. Chem. Soc. (1930) 52: 2702-2712.

samarium ions can exist as two or more "electronic isomers," whose relative proportion depends on the temperature. Such isomers have identical nuclei and identical valences, and differ only in the number of electrons situated in certain shells.

If electrons prove disappointing as a mechanism for the inversion, there is still the possibility of oscillatory versus rotational motion in a group of atoms such as NH_4 or NO_3. Evidence for this explanation has been brought forward by Pauling[32] and by Kracek,[33] and Bridgman[34] shows, by application of the quantum principle, that the anomalous heat capacity at the inversion-point, especially if the inversion is at a low temperature, is consistent with a change of motion of the kind indicated.

Transformations in a Glassy Phase

When we leave the crystalline phases, to which the greater part of this paper has been devoted, and begin the study of the chaotic condensed types of phases (liquid and glass), we find the thermodynamic method of approach relatively barren, so far as systematization or prediction are concerned. To the thermodynamic chemist a condensed chaotic phase of given composition is just a single phase, whether it be hot enough to be as fluid as water or whether it be cold enough to possess the properties of the elastician's ideal solid. We find that a perfect solid can be a chemical-thermodynamic liquid. This seeming absurdity would disappear if we could bring ourselves to drop the term "liquid" in talking about applications of the Phase Rule and substitute the term "chaotic phase" or something equivalent thereto. The facts are in accord; a resilient glassy phase of given composition can attain just as complete an equilibrium with a certain crystalline phase at low temperatures as it can with a certain other crystalline phase at temperatures high enough to liquefy the glass, and yet it remains the same phase, without discontinuity, from low temperature to high. The principal difference between glass and liquid is that the rate of attaining equilibrium is likely to be far slower in the glass than in the liquid.

Recognizing that there can be no "change of phase" in the glassy state, can we not find changes of constitution that correspond, in their atomic and electronic interpretation, with the changes pictured in the crystalline phase? There is plenty of evidence that we can. In the first place, glasses show small departures from a uniform and continuous change of certain properties with temperature, suggestive of the inversions in a crystalline substance. In the second place, the properties of a glass, when carefully measured, are found to be dependent not only on its composition and its existing temperature and pressure, but also on its thermal and mechanical history.

Examples of the first, or reversible effect, are: the rapid change in

[32] Pauling, L., Physical Rev. (1930) 36: 430-443.

[33] Kracek, F. C., Posnjak, E., & Hendricks, S. B., Journ. Amer. Chem. Soc. (1931) 53: 3339-3348.

[34] Bridgman, P. W., Trans. Amer. Inst. Min. Met. Eng. (1931) 96: 17-37.

the thermal dilatation of vitreous silica in the region of the inversions in tridymite and cristobalite; and the almost discontinuous change of heat capacity of various silicate glasses in the vicinity of their softening-intervals.

The second kind of effects, which are either irreversible or only slowly reversible, are those dependent upon the history of the specimen. They are quite small and have gone unnoticed until recent years, but there can be no question as to their existence. They are best expressed as departures from a mean value characteristic of the composition, and are well exemplified by recent measurements of density and refractive index.[35]

Limitations of space prevent any detailed interpretation of these phenomena in terms of leptonic constitution. It need only be remarked that the interpretation will be quite analogous to that in the crystalline phases, because the inter-atomic bonding in a glass is of the same nature as that in a crystal. There is no convincing evidence that will require us to consider a glass as an aggregate of sub-microscopic crystals, although this view has gained some acceptance as a result of recent X-ray measurements on vitreous silica. Vitreous silica is not an aggregate of minute cristobalite crystals; it is vitreous silica, a modification with structure and properties of its own.

Departures from Homogeneity

In closing, I should at least mention another kind of variation which is characteristic of both crystalline and chaotic phases and which should be influenced to some extent by heat treatment, namely: *permanent departures from homogeneity.*

The experiments and theoretical calculations of a number of physicists, including Joffé, Smekal, Zwicky, and others, have brought out the view that while certain properties of crystalline substances, such as density, are but little influenced by structure, certain other properties such as strength and electrical conductivity may be very sensitive to slight irregularities of structure. The hypothesis has been offered that the experimentally known variations of these structure-sensitive properties are due to a superposed mosaic or periodicity in the crystal. The crystal is not a monotonous succession of similarly placed atoms, but is organized more like an army with its regiments and brigades. The smallest regiment contains somewhere between a million and ten million atoms.

In this country, Zwicky and Goetz, at Pasadena, have done most of the theoretical and experimental work in the development of this hypothesis and its consequences.[36] The work has been principally on metals, but the same principles will apply to the ceramic oxides. The so-called "secondary structure" will be influenced by heat treatment,

---

[35] For example, Morey, G. W., & Merwin, H. E., Journ. Opt. Soc. Amer. (1932) 22: 632-662.

[36] See the brief up-to-date review by Mehl, R. F., Trans. Amer. Soc. Steel Treating (1933) 21: 998 (Nov.).

particularly because of the part that must be assumed in it by small percentages of impurities.

Whatever the final form of the hypothesis may prove to be, it can be said in its favor that absolute uniformity and continuity is a rare thing in Nature, and that periodicity is much more likely to be the rule, both in static and in flowing systems.

Glasses, likewise, may reasonably be expected to show permanent departures from homogeneity even though demonstrably uniform in chemical composition. The tendency of silica and silicates to form threads and sheets of indefinite extent is now well established,[27] and these structures can hardly avoid a preferred orientation in any piece of glass that has been mechanically worked. In a well-annealed glass, however, we may expect that the anisotropy will be extremely small, of the order of magnitude of the anomalies in density and refractive properties mentioned in a preceding section.
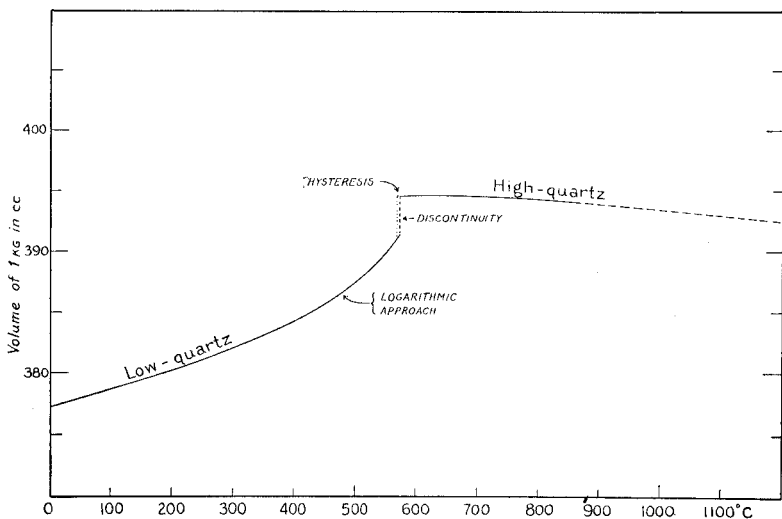
Fig. 1.   Curve of specific volume of quartz against temperature, illustrating the principal characteristics of an alterative inversion.

DISCUSSION

Louis J. Trostel, Chairman

Chief Chemist, General Refractories Company
Baltimore, Maryland

O. A. Knight *(Associate Professor of Metallurgy, The Pennsylvania State College):* I understand from your talk that the A_2 point in iron at 768°C is truly an allotropic point in the sense of a concealed inversion. Is this correct?

---

[27] Bragg, W. L., The structure of silicates (1932, Leipzig).

MR. SOSMAN: "Concealed inversion" is my term for such a change.

PROFESSOR KNIGHT: You mentioned the rapid change of austenite to martensite, and that it was difficult to make moving pictures of the change. I would be glad to know at what temperatures the attempts were made, in view of the fact that I have been doing some work along this line at liquid air temperatures.

MR. SOSMAN: I believe the polishing and etching work was done at higher temperatures (100°C).[1]

N. W. TAYLOR *(Head, Department of Ceramics, The Pennsylvania State College)*: The compounds MnO, MnS, FeO, and Fe_3O_4 would appear to possess inversion of the "concealed" kind at temperatures between 100° and 200°K. Their specific heat curves show marked humps superimposed on the normal ascending trend. The extra specific heat is not confined to a definite temperature but covers a range of twenty or thirty degrees. The curves are rapidly reversible with falling temperatures. I examined the x-ray diffraction patterns of these materials at temperatures over the whole transition range as well as above and below, and found no essential change in structure but only some curious and probably continuous changes in the lengths of the sides of the cubic unit cells.[2] The interatomic forces in these compounds are probably too high to permit ionic rotation in the lattice, and it is more probable that the inversions are connected with certain changes in the electron states. The specific heat and volume effects are very definite and certainly indicate that important changes are occurring within the solid structures.

[1] Wiester, Zeitschr. f. Metallkunde (1932) 24: 276.
[2] J. Chem. Physics 2 58-64 (1934)

Melting and Annealing of Glass

By J. T. Littleton

Chief Physicist, Corning Glass Works, Corning, N. Y.

IT HAS been known for some time that the physical properties of silicate glasses are affected by the heat treatment of the test sample. Fortunately most of the changes caused by differences in heat treatment are of a minor magnitude and do not particularly affect the quality of the manufactured product. However, the subject of changes in glasses caused by thermal treatment is of first order importance to the research worker whose prime problem is that of precision in measurement and who is interested mostly in the question of the constitution of glass.

The raw materials entering into inorganic glasses are first mixed together in their proper proportions, then melted, fabricated to some shape and cooled. It is evident that from the batch stage the entire process of manufacture is one of heat treatment of the raw materials and of the manufactured article. Even after glass has been first formed to one shape, it may be reheated and fashioned into something entirely different, or form a part of something else, as illustrated by laboratory apparatus made by the blast burner, vacuum bottles, incandescent lamp bulbs, radio tubes, thermometers and many other articles. The heat treatment of the glass is an inseparable part of its manufacture. It is proposed to discuss here from the standpoint of the physicist the separate stages of the heat treating processes and their bearing on the properties of glasses.

Melting

Glasses of many varied compositions are melted commercially and experimentally and of course no one temperature schedule is adequate for all glasses; as a matter of fact even the same glass has a temperature-time-schedule depending upon the design of the melting unit; hence a specific melting schedule cannot be a part of this discussion.

It is believed by many that melting consists of, first, a chemical combination of certain of the ingredients, then a fining process, this latter being merely an escapement of entrapped bubbles. Little is known as to the exact chemical combinations taking place in glass during the melting process. The evidence that there are any compounds or silicates formed does not appear to be very conclusive. The recent paper by Seddon, Tippett and Turner[1] points out a relation between specific resistance and composition indicating the formation of the compound sodium disilicate. But in general there seems to be no other evidence of compounds in glass formed during melting and existing at room temperatures.

Howarth, Maskill and Turner[2] explain the solution of soda in glass

[1] S. Seddon, E. J. Tippett and W. E. S. Turner, J. Soc. Glass Tech. 16, 450 (1932).
[2] J. T. Howarth, W. Maskill and W. E. S. Turner, J. Soc. Glass Tech. 17, 25-49 T (1933).

as the formation of soda silica compounds on the surface of the silica grains followed by the gradual solution of the compounds into the glass. At low temperatures the silica grains when first attacked become clouded on their surfaces only but gradually become opalescent. The sodium carbonate is decomposed, and the sodium oxide penetrates the silica and is absorbed by it, perhaps combining with it in definite proportions, but this combination cannot be considered as definitely proven. It may well be that the solution of silica by the soda is merely an absorption process. The silica lattice structure of the sand grains is disarranged by the high temperature and consequent molecular activity and is easily penetrated by the smaller soda molecules, thus causing the fluxing effect, but there is no definite combination of elements in definite proportions characteristic of the formation of compounds. The bonds, if formed, are so weak that they are disrupted by thermal agitations. Melting then would consist of a fine subdivision of all batch particles and a molecular mixing and diffusion of these particles into a homogeneous mass. If there be no definite chemical compounds as such forming during melting, there will be no delayed reactions to be completed, and beyond the effects of degree of homogeneity there will be no effect of the time and temperature of melting on the physical properties of the final product.

Owing to the viscosity of the mixture, this mixing is slow yet surprisingly rapid. Day[3] has shown that approximately 30 minutes at 1500°C is sufficient to form a glass from the raw batch materials which has the final properties of glass melted for much longer times. Figure 1 shows the results of Day on a soda lime glass containing no fining agents.
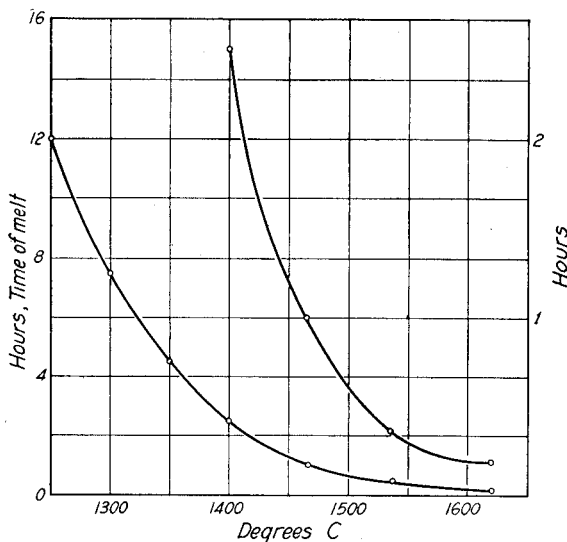

Fig. 1. Melting time of a raw glass batch at several temperatures.

---

[3] R. K. Day, Presented at meeting American Ceramic Soc. Feb. 24, 1932.

The glass was melted in a platinum crucible in an electric furnace having a particularly uniform temperature distribution tending to eliminate the effects of possible convection currents.

If melting of glass be largely a molecular mixing process, it is rather remarkable that this process is so rapid. It is known that an introduced inhomogeneity such as a cord or stone is usually very slowly absorbed by diffusion. The solution of such a cord might take at least several hours or even days. Yet as stated previously the melting process may be complete in only a few minutes. The fact that it is a stone or cord shows that this particular mixture is more resistant to diffusion than the main body of the glass. The diffusion process is considerably aided by the liberation of gas from the batch materials. The large gas bubble in escaping violently stirs or agitates the molten glass and in this manner effectively mixes the materials. Mixing is also assisted by convection currents. The glass is fairly quiescent after the gas evolution is complete and consequently there is no stirring action to break up the cords.

At one time it was believed that the physical properties of glasses were affected by the thermal treatment of the glass in the molten condition.[4] However, later work led to the positive conclusion that the changes in properties observed and ascribed to thermal treatment were due to inhomogeneities and impurities from the dissolved clays of the melting unit causing the formation of a glass of a new composition.

There is still one other factor depending upon melting conditions which might affect the properties of glass and that is the quantity, character and disposition of the dissolved gas. The presence of dissolved gas in glass was first observed by E. T. Allen and E. Zeiss[5]. Dalton[6] has shown that glass at room temperature may contain practically 100 per cent by volume of dissolved gas. While gas content might have considerable to do with the rate of fining and the action of fining agents, the limited study so far made indicates little effect on the physical properties of glass.

The fining of glass is again largely a physical process. The rate of fining of the glass is controlled by the viscosity of the glass, the size of the bubbles, by the action of the dissolved gas and the direction and magnitude of the convection currents. The gas forming process during the decomposition of the batch materials is rather quickly completed. The experiments of Day mentioned earlier showed that glass free of speck could be obtained in thirty minutes time at 1500°C and ten minutes at 1600°C. This means that any process of gas evolution is finished in somewhat less time than this. The old theory that seeds are a product of a chemical reaction which lasted for hours seems to be definitely disproven. Dissolved gas stays in solution unless there be some temperature fluctuation. The phenomenon of "reboil" must be a dis-

[4] J. T. Littleton, "A review of recent progress in the study of the thermal treatment of glass", J. Soc. Glass Tech. 15, 262, 1931.
[5] E. T. Allen and E. Zeiss cited by Sheppard, J. American Ceramic Society 1, 737(1918).
[6] R. H. Dalton, J. American Ceramic Society 16, 425-32, 1933.

solved gas evolution. The exact temperature condition necessary to cause a reboil must depend upon the initial gas content and the past temperature history. There has been no investigation made which will connect in a quantitative manner gas content, temperature and reboil.

Various materials may be added to glasses to assist in fining. The physical and chemical action of glass fining agents are not particularly well understood. The concensus of opinion is that a fining agent is a gas forming agent, liberating bubbles of large size. These bubbles rise rather rapidly to the surface and in rising drag smaller ones along with them. There is also some evidence that a bubble in a glass melt tends to grow in size, that is, dissolved gases diffuse into the bubble thus decreasing the amount of dissolved gas as well as increasing the bubble size and consequently lessening the possibility of seed formation.

Salt cake in addition to its fining action seems to have a direct action on the silica grains. Sand in a glass batch tends to collect in dry lumps just as does flour in water, and salt cake permeates these lumps, separating the grains and thus exposing each surface of each grain simultaneously to the solution processes.

Convection currents in the glass serve to better mix the glass by their stirring action but they may also serve to retard fining since the downward flow of the glass may exceed the gravity rise of the bubbles and hence sweep the bubbles toward the colder portion of the melt and considerably increase the time required for fining. The control of convection currents then becomes a problem of temperature distribution and furnace design.

It is therefore concluded that the temperature treatment of glass during melting affects primarily the quality of the glassware obtained but has no observable effect on the physical properties of the glass beyond that of homogeneity.

Devitrification

After a glass is melted and fined it is worked to some shape. A cooling process proceeds and attends the working process. Below some definite temperature called the devitrification or liquidus temperature the glass will crystallize. If fabrication can be accomplished above the devitrification or liquidus temperature then there is slight danger from devitrification during cooling, since the cooling of the fabricated article is always rapid until the annealing zone is reached. Most glasses will not devitrify in the annealing zone in the time required to anneal.

Dietzel[7] has given some information concerning one family of soda-lime-silica glasses. The observations of Dietzel show there is a temperature of maximum crystallization at roughly 100° below the liquidus temperature and below this maximum crystallization temperature the velocity of crystallization is retarded with decreasing temperature and finally becomes zero. For a discussion of Dietzel's measurements in some detail the reader is referred to recent papers by Littleton and Preston[8].

[7] A. Dietzel, Sprechsaal 62, 506, 1929.
[8] F. W. Preston, Glass Industry 12, 1. 1931.

Instead of measuring directly crystallization-speeds as did Dietzel the tendency of a glass to devitrify may also be evaluated by determining the liquidus temperature and possibly the viscosity of the glass at the liquidus. The technique of measuring the devitrification temperature has been developed and adequately described by Morey and his co-workers. The glasses more fluid at the liquidus are more easily devitrified. It is possible that specifying the viscosity at the liquidus rather than temperature, or the ratio of temperature to viscosity will give a figure more nearly indicative of the devitrification tendencies of the glass. The glass having the highest viscosity at the liquidus temperature should devitrify the most slowly.

The problem of avoiding devitrification is then simply one of determining the liquidus temperature and exceeding this temperature during any protracted heating. Any passage through the devitrification zone should be as rapid as is practical.

If the glass is later subjected to a reheating and re-working process these same principles should be followed. It has often been observed that old glass tubing will whiten when reheated in a gas flame. This action is due to the dissolved water and may be avoided by making a glass having less solubility in water. Lead glasses may also be reduced by a reducing flame giving the appearance of devitrification. However, these are not devitrification phenomena.

In the majority of present day commercial glasses the subject of devitrification is of little importance. If the present available information as to compositions and working processes be applied there is little likelihood of devitrification occurring. The occurrence of devitrification is practically always due to an inhomogeneity in composition. At the particular point of devitrification the glass composition deviates greatly from the average so as to favor devitrification.

The recent comprehensive reviews of the subject of devitrification have treated this subject in considerable detail and it would be mere repetition to consider this question any further in this place.

Annealing

As hot fabricated articles are cooled the glass becomes solid, or too viscous to flow or yield in finite time under forces which are insufficient to cause fracture.

Glass in cooling from a molten state may at the final temperature be left in a strained or stressed condition. The stresses are caused by a differential contraction of parts of the glass with respect to other portions. If, while the glass is sufficiently fluid, a temperature gradient be introduced in it and as it cools this gradient be maintained until it is practically a solid, then as the temperature gradient disappears there will be strain introduced depending upon the temperature distribution at the time the glass becomes solid. Most annealing schedules however aim to bring the glass to a condition of uniform temperature before cooling begins and at this temperature to release all the internal stress,

then to cool the glass so that no objectionable additional stress will be introduced during cooling. During this cooling there is a temperature gradient introduced, and if there be a yield in the glass due to these temporary stresses, then in the final state as the gradient disappears the amount of strain released by the viscous yield will reappear, but, of opposite sign. The physical explanation of strain, its cause and removal have been described by many others and no repetition of that is needed here. The glass manufacturer is mostly interested in the economics of producing ware so annealed that its service will be satisfactory; while the scientist is interested in the exact laws of annealing and in what happens in the glass during this process. It is in this temperature zone that the glass changes from a noticeably fluid body to a solid unyielding substance. It is natural to expect that if its properties in the solid state are affected by a temperature history in some upper temperature level this zone of change to a solid would be the most effective temperature zone in affecting the properties of the glass. Yet in spite of this natural presumption, it has been only in the last 15 years that the changes in the properties of glasses taking place during the annealing process have been investigated to any considerable extent.

Since the work of Adams and Williamson and of Hampton, it can be stated that so far as the practical annealing of commercial glass ware is concerned the problem is simply one of temperature control. Fine annealing of such ware is not required and is even not desirable in many articles. However in optical ware and large lenses or mirrors it is believed to be necessary. But even in this field there has been no work done which indicates the necessary degree of annealing. Many optical grinders state that if the strain be symmetrical it will give the desired results even though its intensity be high. But besides the mere release of strain during annealing there is a change in the physical constants of glass caused by the prolonged heating. The exact laws of strain release are of more theoretical interest than of practical importance (very large glass objects excepted) since by an understanding of these phenomena we are able to arrive at more definite conclusions as to the constitution of glass. Accordingly the studies of the effects of the thermal treatment of glasses in the annealing zone can be separated into two parts, (1) rate of strain release (2) effect of thermal treatment on physical properties. These two divisions are, as will be seen, not entirely separated one from the other.

Rate of Strain Release

As mentioned earlier the process of annealing may be separated into two parts one relieving the stress at constant temperature, the other cooling the glass so that no objectionable stress is introduced. In practice the latter treatment is more difficult to control than the former. Physically however, it becomes a problem in heat conductivity plus that of strain release, and if the problems of strain release are solved the cooling problem is then capable of solution. Accordingly only strain release or relaxation laws are discussed here. The equations hitherto developed giving the relationship between strain release and time at any

constant temperature are only approximate. As said before they are very satisfactory for ordinary sizes and shapes but are not so satisfactory for larger objects. Most of the present difference of opinion has to do with how the rate of annealing varies with the stress.

If glass be a purely viscous fluid during annealing at constant temperature, then as deduced by Maxwell df/dt=kf/η where f is the stress, η the viscosity and k a constant for the given glass at the given temperature. Adams and Williamson found experimentally that df/dt did not vary as f but as f². Existing theories and observations are based on the assumption that viscosity is constant at a constant temperature, that is, does not change with time. Lillie has shown however that viscosity does change with time. The time rate of change of viscosity is not a simple affair and the introduction of this factor into annealing equations leads to a fairly complex expression somewhat difficult to handle analytically. However, it must be the failure to take into account this time change of viscosity which has caused the discrepancies between theory and observation.

The change in viscosity with time is an equilibrium attaining process similar to the changes in expansion coefficient, density, refractive index, specific heat and electrical conductivity previously observed. Berger[9] has reviewed the data in the recent literature on these effects. Littleton[10] has attempted to show that these changes do not occur at a fixed definite temperature but are changes resisted by the viscosity of the glass, hence at low temperatures they occur very slowly but as the temperature is increased the changes become sufficiently rapid so that they are observable in the time of the experiment. If the rate of temperature increase be rapid the change will appear to occur suddenly. The measurements have usually been made on the properties of glasses while they were undergoing changes in their equilibrium and there is not much information bearing on the properties of glasses when fully stabilized at different temperatures.

Viscosity at constant temperature changes with time at a rate depending upon both the temperature and the previous thermal history of the test piece. The phenomena behave as though the viscous condition belonging to some previous temperature condition was frozen into the glass and time was required for the glass to change over from its former state of fluidity to that characteristic of the new given temperature. A glass suddenly cooled is initially more fluid, but a glass after being held at one temperature for some time and then having its temperature suddenly increased is initially more viscous. In the first case the glass gradually gets stiffer, and in the second case the glass becomes more fluid as its temperature is held stationary. The curves in figure 2 show the magnitude of this change. The newly drawn fiber increases in viscosity by a factor of 10 and the glass previously stabilized at 478° decreases in viscosity by about a factor of 5.

The laws of change of viscosity with time have not been accurately

[9] E. Berger, J. American Ceramic Society 15, 647-77, 1932.
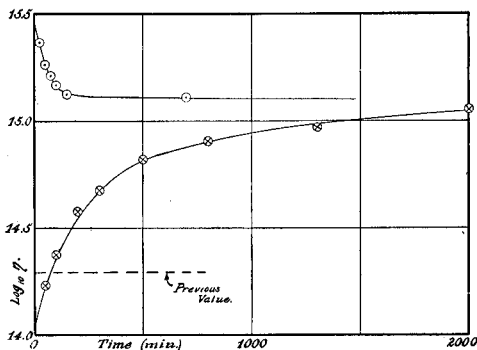[10] J. T. Littleton Ind. and Eng. Chem. 25, 748-55, 1933.

Fig. 2. Time change of viscosity of glass fibers.

determined. The above curves simply represent the viscosity change with time in the case of a glass initially in some unknown state of equilibrium. This initial state will depend upon the temperature from which the glass was cooled and also upon how rapidly it was cooled to its final state. The change of viscosity at constant temperature is then a variable, since the initial state is a variable. This initial state of the glass can be controlled to a degree by careful control of the experimental conditions. In practice, however, the conditions are much more com-plex. The cooling rate depends upon the dimensions of the article and the local cooling conditions. These conditions vary and cannot be duplicated in an experimental sample. In other words while it is possible to measure accurately the time-viscosity relationship for a series of glass test specimens having known thermal histories it is not possible to identify the thermal history of a glass article with the proper time viscosity curve so that the changes in viscosity with time can be applied to compute the rate of annealing of the glass article. Nevertheless it seemed worthwhile to make an attempt to apply viscosity-time observations to a strain release measurement in order to determine whether there be any relationship between the two. Since no data are available on any one glass showing both the change in viscosity with time and the rate of strain release, it became necessary to make such measurements.*

Figure 3 represents the observations on strain release of two samples of the same glass annealed at two different temperatures. At the top of the figure is given the temperature schedule and the initial strain release data plotted on an enlarged scale.

It is evident from Figure 4 that the rate of change of stress is pro-portional to the square of the stress in accord with the Adams and Williamson equation.

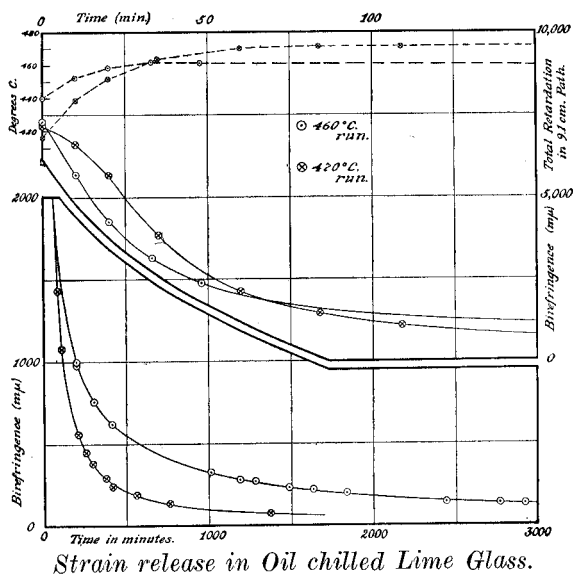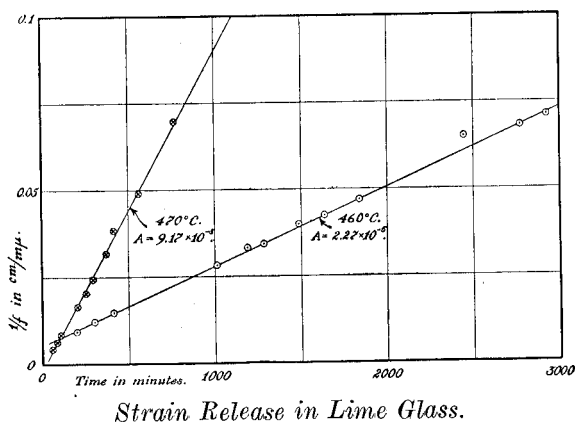*Strain release in Oil chilled Lime Glass.*

Fig. 3.

Strain Release in Lime Glass.

Plotted as required by: $\dfrac{\delta f}{\delta t} = A f^2$.

Fig. 4.

In order to evaluate the instantaneous viscosity of the glasses, it was necessary that the viscosity measurement follow the temperature schedule of the annealing test. Accordingly the viscosity test specimen was inserted in a furnace having its temperature the same as that of the annealing temperature furnace at the start of the annealing run and the temperature was increased at the same rate.
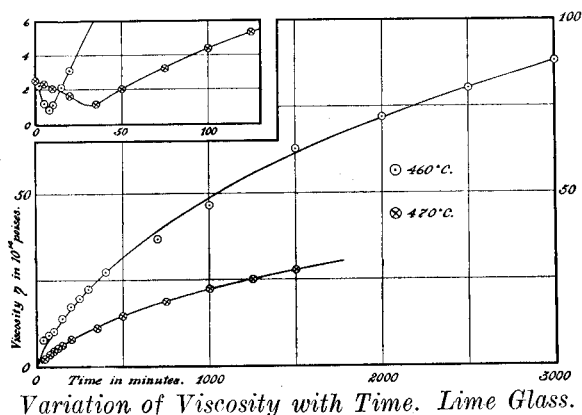
Variation of Viscosity with Time. Lime Glass.
Fig. 5.

Figure 5 represents the viscosity change with time of the glass at the two temperatures. Since in the annealing test the temperature did not reach its final value until about 40 minutes the same procedure was followed in the viscosity run. The enlarged scale in the upper left hand corner of Figure 5 shows the change in viscosity during the changing temperature interval. The lower curves are all at practically constant temperature.
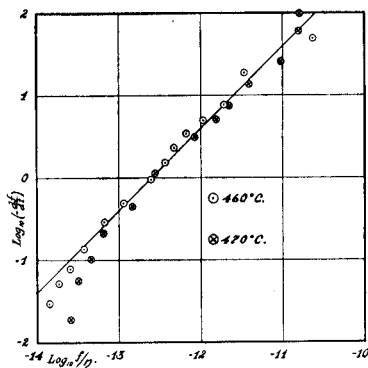
Graph showing relation: $-\dfrac{\delta f}{\delta t} = 6.7 \times 10^{10} \dfrac{f}{\eta}$.

Fig. 6.

From the curves in Figure 5 η is obtained for different times. In Figure 6 the log f/η is plotted against the log of df/dt. It is seen that this relationship is fairly linear. However in order to allow for the time required for the annealing specimen to come to constant temperature the zero time of the viscosity run was taken 30 minutes ahead of the annealing time zero. The slope of the curve is unity, consequently the equation of the graph is

$$- \, df/dt \, = \, 6.7 \times 10^{10} \, f/\eta$$

The constant 6.7×10^{10} has the dimensions of an elasticity coefficient.

For glass the shear modulus at room temperature is roughly 2.8×10^{11} which is greater than 6.7×10^{10} by a factor of 4. Numerically then

$$- df/dt = Gf/4\eta$$

where G is the shear modulus of the glass at room temperature. Just what G is at the annealing temperature is hard to say, but it is not probable that it is as small as one fourth the room temperature value.

This equation for the rate of annealing of glass is physically understandable but not simple to apply.

It is apparent that probably df/dt does vary as f/η. The inability to get a better experimental verification of this conclusion is no doubt due to the inability to identify the proper viscosity change curve to apply to the strain release sample. Very probably there can be no proper viscosity curve to apply to such a sample. The viscosity of the viscosity test specimen, a small glass fiber one millimeter in diameter, is probably fairly homogeneous throughout the sample, while in the annealing test piece the viscosity probably varies from the surface inwards, since the cooling rates of these portions of the glass varied considerably one from the other.

Accordingly one is forced to the conclusion that while annealing phenomena obey viscosity laws in a rather simple manner it is not possible to apply viscosity data to annealing laws so that annealing rates can be exactly computed. If the viscosity-temperature curve for a glass be available, as well as information on the time rate of change of viscosity, then it is possible to compute an annealing schedule without making annealing measurements. For practical results however the Adams and Williamson empirical equation, that rate of release of stress is proportional to the square of the stress, is satisfactory and convenient to use. For high and low stresses this law is not true but an empirical correction can be applied for those conditions where further refinement is necessary. For the best results an annealing rate curve should be obtained for the glass in question at the temperature at which the glass is to be annealed.

There has been considerable doubt as to what effect viscosity has on annealing. It has even been questioned whether it has any effect. These results seem to show conclusively that annealing of glass is a viscous flow phenomenon, the rate of release of stress for unit stress being inversely proportional to the viscosity.

DISCUSSION

Louis J. Trostel, *Chairman*

E. L. Hettinger (Willson Products, Inc., Reading, Pa.): No one can question Dr. Littleton's statement—"the subject of changes in glasses caused by thermal treatment is of first order importance to the research worker." Another statement, "The heat treatment of the glass is an inseparable part of its manufacture," is not appreciated by

a great many of the manufacturers. The references to the ''viscosity of the mixture and the rate of fining of the glass being controlled by the viscosity of the glass,'' cannot be ignored.

Under the ''Rate of Strain Release,'' I fully agree with Dr. Littleton that ''the cooling of the glass so that no objectionable stress is introduced,'' is correct. It may be difficult to control, but where the *objects are of uniform size,* it is quite an easy matter.

While the cooling rate does depend upon the dimensions, it is also well to bear in mind the *irregularities of the object that is being cooled.* This leads to more difficulties than mere size.

Perhaps the most important is the last paragraph, ''there is a relation between the viscosity of the glass and the annealing or the heat treating of the same.'' This statement is based upon some work covering 4,000 pieces of light crown soda lime glass with a fairly high viscosity.

Petrography and Heat Treatment of Chromite Refractories

BY GILBERT E. SEIL

Technical Director, E. J. Lavino and Co., Philadelphia, Pa.

I HAVE been requested by Dr. Taylor to discuss before you, and I hope later with you, the petrography and heat treatment of chromite.

To me this has been a most interesting and fascinating study and has occupied the major portion of my time for the past eight years. The organization with which I am connected has spared no expense in allowing me to purchase and install any type of optical, physical and chemical equipment required for this work, and has given me a free hand in procuring the proper personnel for assistance.

This paper, as originally written, seemed to place petrography in the position of a universal tool with which to conduct and to evaluate research. This is not true. Although the laboratory work which, of course, is purely experimental, is of great value to us, it cannot and does not solve industrial problems by itself. It does however, furnish leads from which semi plant or plant size experiments can be made. These large scale experiments are the next step in development after the laboratory work has been completed. However, even plant scale experiments are not sufficiently conclusive, though they be conducted with the most careful consideration of the laboratory results. An approximate answer can be arrived at only after the products of the plant scale experiments have been tested in actual industrial installations.

At this point it may be well to remark that a single experimental application of a refractory material is only indicative of its possibilities, and is in no way conclusive, even though only a single field of application is being considered. Slight variations in the method of furnace operation, a small change in the mechanical structure, the use of a cement physically or chemically unsuited for the particular refractory, and the method of using the cement, may cause such effects that the pictured value of the refractory body may be misleading.

Our experiences in the laboratory, in the plant, and in practice, are such that a most definite and emphatic statement must be made now. A majority of the failures of refractory bodies is due to the method of installation, and not to the refractory itself.

The proper installation of refractories controls the isothermal lines in the individual piece and the isothermal plane in the refractory body taken as a whole. These isotherms control movements due to temperature alone, and also control chemical and physical rearrangements which take place in some refractories no matter how well they may be manufactured. They also partly control the rate of slag penetration, and

the rate at which the slag reacts with one or more components of the refractory body after penetration.

Theoretical Discussion

The above discussion is a brief survey of refractory research, although the general plan followed does not vary particularly in any field of industrial research. Most research is carried on haphazardly by men with varying degrees of preparation for this type of work, and with varying knowledge of natural laws and their application to the individual problems. Many of these research workers, if they plan at all, plan their work haphazardly and may or may not arrive at an answer to their problem. When the work is completed, there is no reason to believe that the answer is final, there may be many methods of solving the problem. All that they find is *a* method which may or may not be the best or the worst. The worker who has a definite method of research which he arrived at through careful study and preparation, not only finds a series of methods of solving his problem, but he has an opportunity, after he has tried these methods, of comparing them from scien tific and economical viewpoints. It may be necessary for him to compromise and so modify the scientific considerations that the results of his work are economical. In an experience of more than twenty years of industrial research there is not one case in which some compromise was not required for economical reasons. In the particular field of chrome refractories the results of purely scientific research can not be applied without such consideration as the supplies of the particular ores that occur in nature, the prices of the ores, the availability of the ores, the stocks on hand, the equipment available for carrying out the process, and finally the known methods of control. Quite often it is necessary not only to solve a problem scientifically but it is also necessary to develop new types of control equipment.

Inasmuch as there are many students who will enter research and many young graduates who have just entered the research field present, I do not believe it out of place to say that most research problems are undertaken before enough information has been obtained concerning the physical and chemical properties, and the sources of supply of the crude materials from which the finished products are to be prepared. Very often the research department is weak in its knowledge of the type of equipment available and necessary for carrying out the methods developed by that department. In my opinion knowing the chemistry and the physics of the research problem is no more important than knowing the types of equipment and the source of equipment in which such chemical and physical rearrangements can be made to take place.

The most important single item in the research field is the definite and distinct statement of the problem. This statement must be most exact and limiting. If a research department is given a problem to make a chrome brick without a definite and precise statement of the properties of the desired product, it is a most indefinite problem. The research department must know exactly what is expected of this brick

in industry. It must state what properties are necessary in the brick so that its performance will meet the requirements for that particular use. This not only entails a definite knowledge of the raw materials from which the finished product is to be made, but also entails a detailed knowledge of the construction of the apparatus in which it is to be used, and at least a fair knowledge of the art in which the apparatus is to be used. As a concrete example: A problem submitted to the research department of E. J. Lavino and Company stated definitely that a method was to be developed for the manufacture of a chrome brick which would withstand temperatures far beyond anything known industrially up to that time, resist deformation under load, minimize slag penetration and be stable physically and chemically.

Naturally the source of raw materials was limited to the available chrome ores. Unfortunately very little was known about the composition of chrome ores, practically nothing of value to this problem had been published. The published petrography of chromite dealt only with raw ores. Our chemical and analytical data was quite complete. We had in our files, chemical analyses of chrome ore from every commercially available source. This chemical data did not give us any indication of how the various elements were combined. We, therefore, obtained samples of every type of ore and found that the African Rhodesian ore contained thirteen different ore structures, that the ore was entirely different from the structures of the African Transvaal ore and the African Lalapansi ore. We also found that the Cuban chrome ore differed materially from the Grecian chrome ore, and that the Grecian chrome ore differed from the Turkish chrome ore although these three chrome ores were quite similar in structure, but quite different analytically. We found that the Indian chrome ore and the Brazilian chrome ore were quite similar but entirely different from any other ore. We did, however, find a most important fact. All chrome ores were composed of two definite and distinct components.

Primary Component

The primary component which is usually between 75 per cent and 90 per cent of the ore is chromite. Although mineralogy tells us that chromite is an iron chromite composed of one molecule of ferrous oxide (FeO), and one of the chromic oxide (Cr_2O_3), crystallized and in the spinel group, we have never in our experience found such a chromite. We do find, however, that in the primary component of all chrome ores a portion of the iron oxide (FeO) is replaced by magnesium oxide (MgO), and a portion of the chromic oxide (Cr_2O_3) is replaced by aluminum oxide (Al_2O_3) in the chromite. This phrase, ''in the chromite,'' is most important because most of the ores contain small amounts of iron, small amounts of alumina, large amounts of magnesia, and large amounts of silica in the secondary component. No ore was found in which the chromite contained silica. The primary component of chrome ores is a chromite composed of ferrous oxide (FeO) and magnesium oxide (MgO) as bases, and chromic oxide (Cr_2O_3) and aluminum

oxide (Al_2O_3) as acids, in which the molecular sum of the bases always equals the molecular sum of the acids.

Secondary Component

The secondary component is magnesium silicate, usually quite pure, sometimes contaminated with slight amounts of iron and alumina, and in a few cases boron. Titanium, manganese, nickel and several other elements have been found in chrome ores, but the percentages are so low that they do not influence the physical and chemical properties of the secondary component.

It is quite essential that the physical and chemical properties of each component are accurately known. In order to determine whether there is a possibility of reaction between these two components it is also necessary to know whether or not these components have any physical influence one upon the other. Does component one recrystallize from component two and is there sufficient component two present to make this recrystallization serious?

Properties of Components

The primary component in commercial chrome ore is a definite chemical entity whose properties vary considerably with its composition. The percentage of iron oxide which has been replaced by magnesia has a definite effect upon the reactivity of the chromite, although no chromite with which we are familiar reacts at low temperatures. They are all almost insoluble in analytical solvents although very finely ground chromite on prolonged boiling with perchloric acid will dissolve, yielding a solution which contains chromic acid (CrO_3) and the other elements in their oxidized forms.

The substitution of aluminum oxide (Al_2O_3) for chromic oxide (Cr_2O_3) in the acid portion of the spinel as far as we have been able to learn has very little effect upon the reactivity as long as the chromic oxide (Cr_2O_3) equals the aluminum oxide (Al_2O_3) molecularly. We also find that the more closely the chromite approaches $FeO.Cr_2O_3$, the more susceptible the ore is to oxidation and decomposition at high temperatures. Physically the fusion point of the chromites is beyond the limit of usual commercial equipment. The chromite is not effected by carbon monoxide as far as reduction to metal is concerned. The reduction of chromite to metal with carbon is only possible when incandescent carbon is in contact with chromite and only takes place at high temperatures.

Physically the primary component chromite can be recrystallized at very high temperatures rather rapidly. The recrystallization, particularly after the crystals are much increased in size, decreases their reactivity because it decreases the surface available for chemical action. In no case have we found an impure chromite. In using the term chromite we wish to differentiate between the primary component of chrome ore and chrome ore. The term chromite does not in any place in this

discussion refer to chrome ore, but always refers to the primary component of chrome ore.

To summarize the properties of the primary component in chrome ore, we can say that chromite is a chemical entity of definite crystalline form in which the molecular percentage of MgO and FeO equals the molecular percentage of Cr_2O_3 and Al_2O_3. It has a melting point of approximately 4000°F and comprises from 75 per cent to 90 per cent of the chrome ore. It is to all intent and purposes, chemically inactive.

The secondary component in chrome ore consists of magnesium silicate in varying states of crystallization. In more than 1000 thin sections and unnumbered powdered sections we have but once found a chrome ore in which the secondary component contains free silica. The ore in which this was found occurred in Rhodesia in South Central Africa. All other chrome ores contain magnesium silicate in which the proportion of magnesia to silica varies from $3MgO.2SiO_2$ to $2MgO.3SiO_2$. Many of these magnesium silicates alter after the ore has been mined and cause the lumps to disintegrate. This alteration in the secondary component in no way changes the primary component. The magnesium silicates are not always pure, sometimes they contain slight amounts of impurities. Up to the present time we have found the following magnesium silicate minerals in the secondary component of chrome ore:

|		
Clinoenstatite	—	$MgO.SiO_2$
Enstatite	—	$MgO.SiO_2$
Forsterite	—	$2MgO.SiO_2$
Parasepiolite	—	$2MgO.3SiO_2.4H_2O$
Chrysotile	—	$3MgO.2SiO_2.2H_2O$
Antigorite	—	$3MgO.3SiO_2.2H_2O$
Talc	—	$3MgO.4SiO_2.H_2O$
Hypersthene	—	$MgO, FeO).SiO_2$
Serpentine	—	$3MgO.2SiO_2.2H_2O$
Sepiolite	—	$2MgO.3SiO_2.2H_2O$

These magnesium silicates, with melting points varying from 2300°F to 2600°F, cause almost all the difficulties encountered in the use of chromite refractories. As soon as the ore is heated to the melting point of this secondary component, the secondary component is converted to a glass which differs from the original crystal in its method of softening. Crystalline substances differ from glasses in their methods of melting, particularly in the range of temperature required to change from the solid state to that of a mobile liquid. In a crystalline body this change occurs at a definite temperature. In glasses this range varies considerably. Magnesium silicates are quite active chemically at high temperatures. They are not in any way stable either physically or chemically and are the disturbing components in refractory bodies made of chrome ore.

To summarize—the secondary component in chrome ores is usually composed of magnesium silicates, the individual piece of ore may contain

several different magnesium silicate minerals varying in composition from $3MgO.2SiO_2$ to $2MgO.3SiO_2$ with melting points between $2300°F$ to $2600°F$, and comprises from 25 per cent to 10 per cent of the raw ore They are chemically active and alter even under atmospheric conditions.

Effect of Relative Placement of Components

We now know that chrome ore is composed of two components, have approximately determined the percentage and the chemical and physical properties of each of these components, and we have made a fair start in our study of chrome ore.
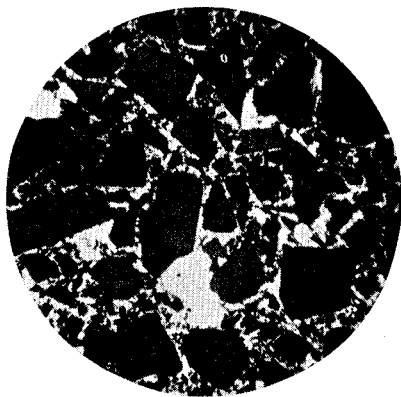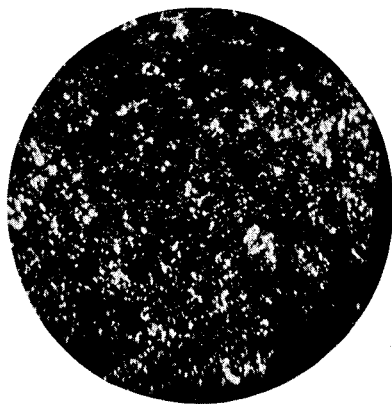
Upper left—Fig. 1.   Crude Chrome Ore—Particles of both components are very small and are almost homogeneously distributed.

Upper right—Fig. 2.   Crude Chrome Ore—Particles of primary component are intermediate in size, with secondary component well distributed in bands of appreciable size.

Lower left—Fig. 3.   Crude Chrome Ore—Particles of each component are relatively large.

Lower right—Fig. 4.   Crude Chrome Ore—Primary component highly crystallized.   Each particle of chromite is surrounded by heavy bands of magnesium silicate minerals.

In studying the thin sections of ores from various mines, and even from various parts of the same mine, we find a variation in the size of the individual chromite crystal, and in the placement of the secondary component. Both of these factors have an important bearing on the manufacture of refractories from chrome ores. If the ore is composed of large chromite crystals surrounded by heavy bands of a low melting point secondary component, there must be a change in the shape of the original body when it is heated to the temperature at which the secondary component alters, softens or melts. On the other hand, if the chromite crystals are relatively small and the secondary component is so well distributed that it covers the chromite with layers which are infinitesimally small, the physical change due to heating is hardly perceptible.

In raw chrome ores this placement of the secondary component in reference to the primary component varies to a maximum extent. It so happens in the commercially available chrome ores the most inactive chromites occur in such a physical condition that the secondary component causes difficulties when this ore is used for refractory purposes. An example of the difference in raw ores is shown by comparing refractory bodies, the first of which is prepared from an ore which contains 80 per cent of chromite and 20 per cent of gangue, in which the gangue is almost homogeneously distributed around and about the very small chromite crystals. Geologically the assumption is that this ore of igneous origin cooled rapidly. The second refractory body is prepared from ore which contains 90 per cent of the same type chromite and 10 per cent of the same type of secondary component. In this case the ore cooled very slowly, the chromite crystals are probably 200 times as large as in the first ore and the secondary component is made up of bands of large dimensions. The bands in this second case are so wide that there is an appreciable distance between the individual chromite crystals and when this ore is heated sufficiently the secondary component undergoes a physical change and deforms the refractory body.

It is safe to say that the secondary component is responsible for the inherent physical weaknesses of the refractory bodies made from crude chrome ore, and for the physical and chemical rearrangements which occur during the burning stage of the manufacture of these bodies. The secondary component is partly responsible for variation in the pore size, pore shape, and pore distribution; for the sagging of the refractory at high temperatures both under its own weight and under added weight; and for the tendency to spall.

The foregoing discussion has covered briefly what the chemical and petrographic examination of various chromites has revealed. The following discussion will show how this information has been applied.

Application of Petrographic Data

Inasmuch as the secondary component is responsible for most of the undesirable properties in chrome refractories, the first thought which occurs is that an effort be made to remove this component. The question arises whether it is better to remove all this component or only a part

of it, for some secondary component is essential to bond the chromite crystals in the finished body. From a purely scientific viewpoint it is far preferable to remove all the secondary component and replace what is necessary to bond the chromite, either in its original state or in a corrected state. There is also the possibility that it may be preferable to use an entirely new bonding material.

Unfortunately we find that from an economical viewpoint it is impossible to remove all the magnesium silicate. Sufficient magnesium silicate always remains associated with the chromite to furnish the glassy bond. However, in the study of refractories it is found that bodies with glassy bonds do not withstand load at high temperatures but that bodies
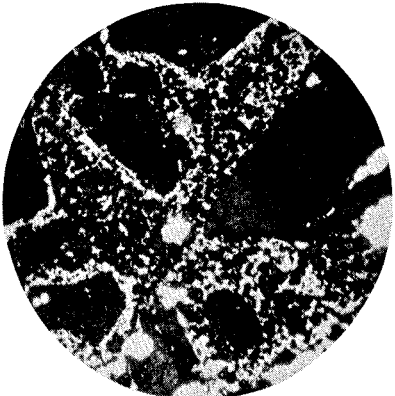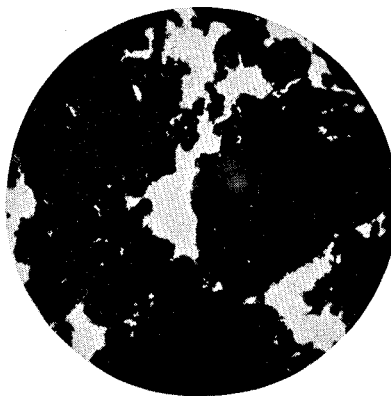
Upper left—Fig. 5.   Heat-treated Chrome Ore—Secondary component completely crystallized as clinoenstatite.
Upper right—Fig. 6.   Treated Chrome Ore—Secondary component completely removed.
Lower left—Fig. 7.   Crude Ore Brick—Secondary component converted to glass and is invisible.
Lower right—Fig. 8. Chrome Brick—Prepared from physically and chemically corrected chrome ore.   Each grain of the primary component (chromite) is completely surrounded by the secondary component, which is crystallized and bolstered forsterite.

with crystalline bonds withstand loads up to the melting point of the crystalline bond. The Critical Tables contain a curve showing the stability of various magnesium silicates and their melting points. Forsterite, composed of two molecules of magnesia and one of silica, if properly prepared and bolstered, would be a suitable crystalline bond. If all the magnesium silicates are converted to forsterite, the quantity and the placement of this new secondary component is important.

A series of experiments was undertaken to determine the effect of heat treating the chrome ore from which a portion of the magnesium silicate had been removed. Specimens of various types of chrome ores were heated and held at various temperatures until an equilibrium was reached, they were then carefully studied petrographically. By this method each point at which a chemical and physical rearrangement took place was carefully noted and studied. A very careful time-temperature curve was developed for the heat treating of physically improved chrome ore to correct the placement and relationship of the first component to
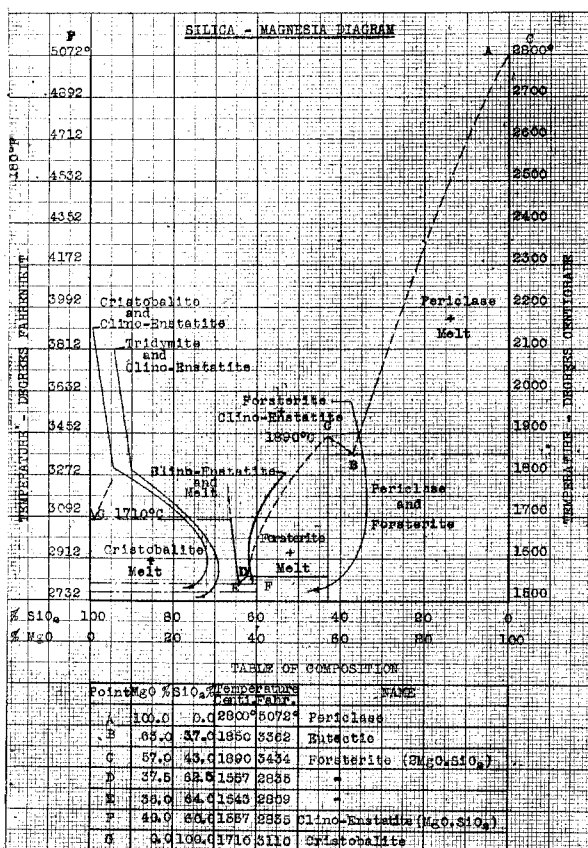

Fig. 9.   Melting temperature diagram for silica-magnesia.

the secondary component. Refractories manufactured from the improved chrome ore were far superior to the chrome refractories manufactured from crude ore. This brick, however, did not solve the problem which was put to the research department. It was necessary to correct the secondary component in the improved chrome ore so that the bond in the finished brick would be crystalline instead of being glassy.

This was accomplished by converting the low melting point magnesium silicate to a bolstered forsterite and the result of this experimental work is the Kromag Brick, which has physical properties and chemical properties far superior to the refractory bodies made of crude ore or from physically corrected ore. Refractory bodies made of crude ore have never been burned commercially at temperature higher than 2700°F. Brick made of physically improved and heat treated chrome ore can be burned at a temperature of about 2800 to 2850°F depending upon the treatment. Refractory bodies made of chrome ore corrected chemically and physically are being burned at a temperature of 3200°F. These temperatures in themselves indicate the changes which have been made in the refractory bodies due to the treatments.
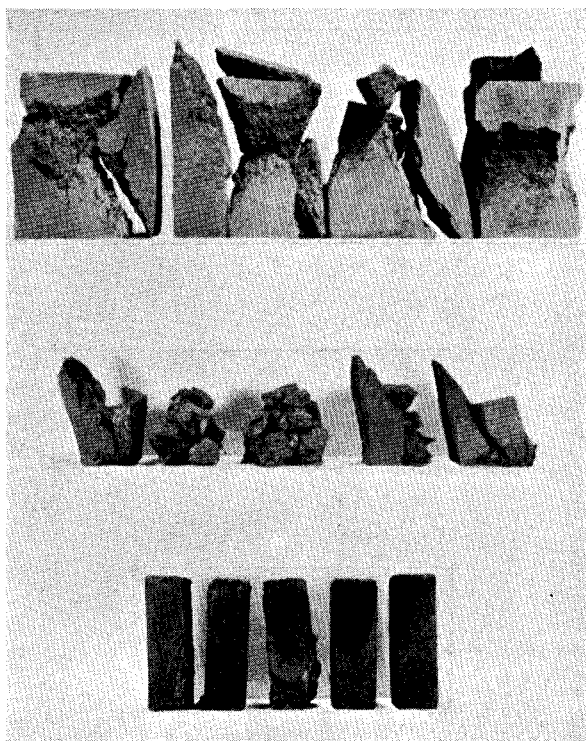

Fig. 10. Deformation under load of 25 lbs. per square inch.
Upper—Brick made from crude ore, 2400° F (1316°C)
Center—Brick made from physically corrected ore, 3000°F (1649°C)
Lower—Brick made from physically and chemically corrected ore, 3000°F (1649°C)

Incidentally it has been necessary for the Research Department to develop a burning curve for these refractories in which the time-temperature relationship is most carefully controlled. In order to control the calorific absorption of the brick it was necessary to develop a method of fuel addition to the tunnel kiln which was constant and yet controllable. It was found that the rate of B.T.U. input is as important as the temperature at which the refractory is burned. In other words the heat absorption of the brick before it reaches the burning zone is most important because it controls the temperature differential between the center and the surface of the brick, and controls the rate at which the final heat is absorbed. The temperature differential from the center to the surface of the brick is very important and is influenced by many things besides the B.T.U. input. The method of making the brick, the particle size, the mesh ratio, the surface condition of the individual particle, the type of pore, the size of pore, the placement of the pores, the pore wall, all have an influence on the rate of calorific absorption. They also have a great influence upon the properties of the finished refractory body. The method of tempering, the method of pressing, the length of dwell of the press, all influence the properties of the finished body. These properties, however, do not influence all refractories to the same degree or in the same manner. The relationship between the various components in a refractory body, influences the effect of changes in the particle size, the particle shape, etc. used to manufacture a refractory body.
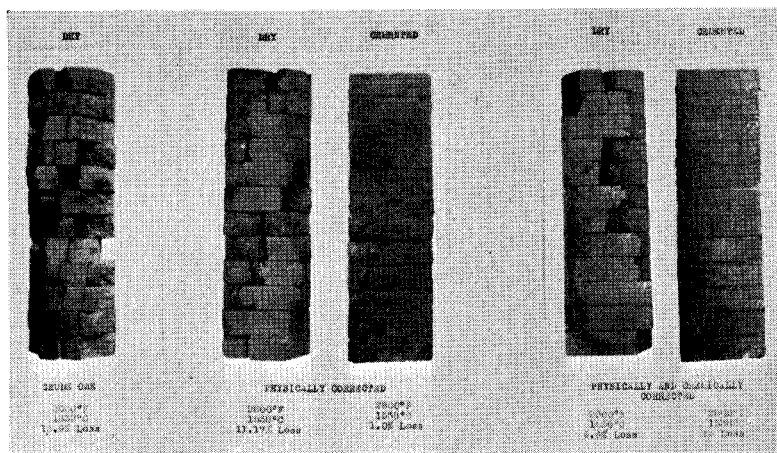

Fig. 11. Comparative spalling tests, chrome brick. From left to right: Crude ore, dry, 2000°F, 1093°C, 15.9% loss; physically corrected ore, dry, 2800°F, 1538°C, 11.17% loss; physically corrected ore, cemented, 2800°F, 1538°C, 1.0% loss; physically and chemically corrected ore, dry, 2800°F, 1538°C, 6.6% loss; physically and chemically corrected ore, cemented, 2800°F, 1538°C, no loss.

Conclusion

As a conclusion several slides will be shown but first a description of an instrument which was developed in our laboratory and which was

manufactured by Bausch and Lomb will be given. With this instrument the points at which physical and chemical changes take place in refractory bodies during heating, a proper time temperature curve for plant practice, and accurate expansion curves for various refractories can be determined.

This instrument is comprised of parallel twin microscopes each with a focal length of 24 inches, so mounted on a base that the distance between them is fixed. Each microscope consists of an achromatic objective lens having a focal length of about 7 inches and a filar micrometer eyepiece. The filar micrometer eyepiece consists of a movable hair line, the position of which can be read in thousandths of an inch, and a 12.5X focusable eyepiece. The hair line is moved across the field by the rotation of a drum which is graduated in 100 parts where each part represents 0.001 inches. The microscope objective lens is placed about 24 inches from the nearest surface of the brick which is located in a muffle with two sight holes through which the microscopes are focused. Since the objective lens may be subjected to some heat which
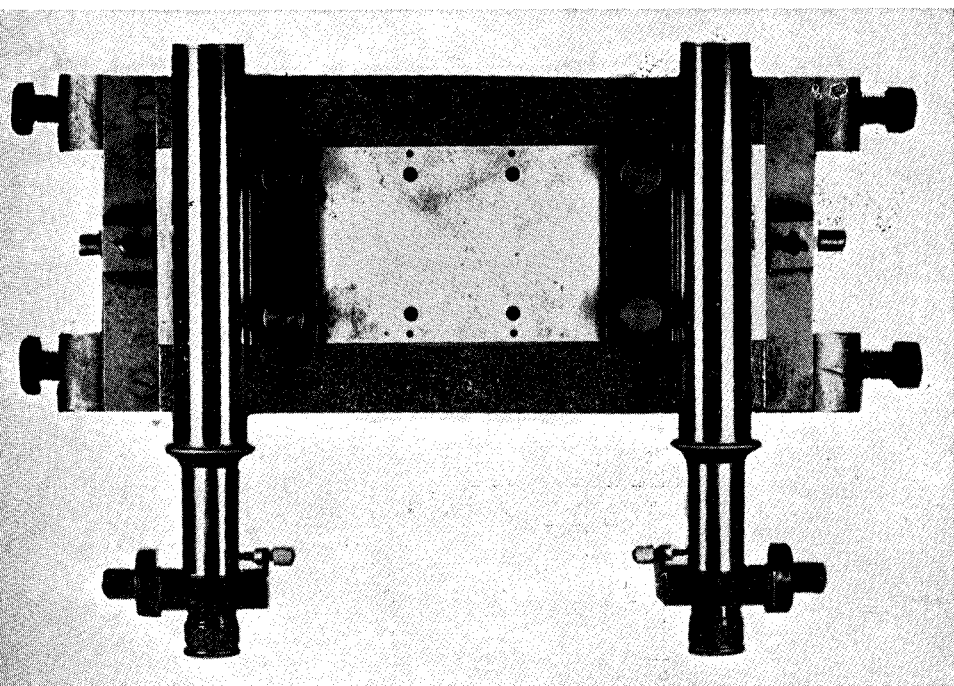

Fig. 12. Parallel twin microscopes with filar eyepieces.

would cause an ordinary cemented objective to deteriorate, they have been made of the air space type. After the instrument has been rigidly placed, it is calibrated with a standard micrometer. The brick is then placed in the furnace so that the edges are visible. At low temperatures

it is necessary to illuminate the ends of the brick so that the movable hair line can be brought into the proper position on the edge of the brick. The readings are taken every fifteen minutes until four readings show no variation at any one temperature. The temperature is then raised to the next point and held there until four readings again show no variation. In this manner a full brick is used for determining the physical and chemical changes which occur in the green brick, and for determining the expansion curve of the finished brick. On the curves which will be projected you will note the number of hours required to reach each point on the curve. Usually three to four weeks are required for a complete measurement.
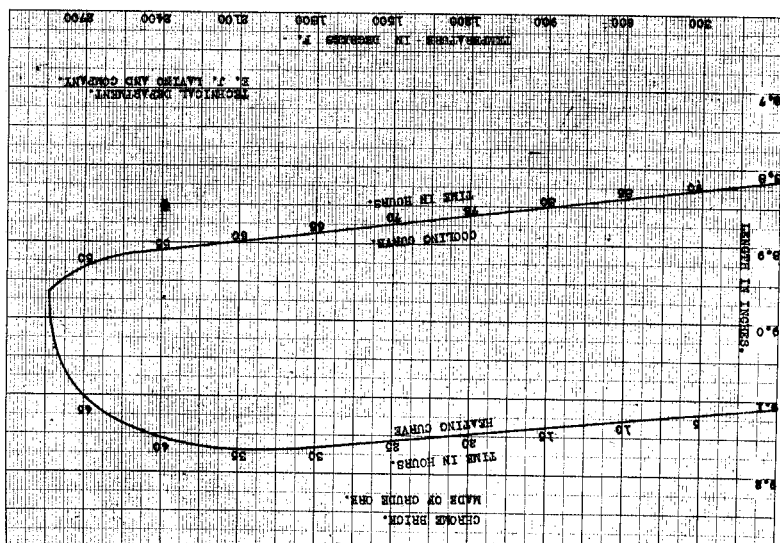
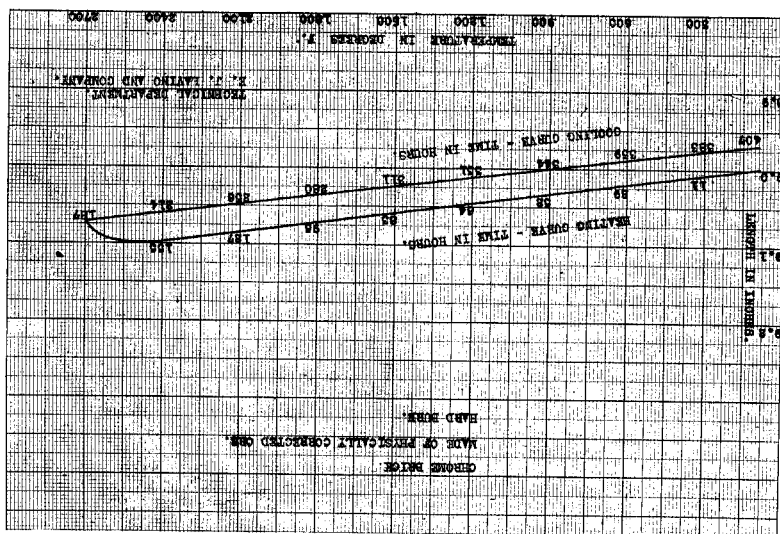**Fig. 13.** Expansion curve—chrome brick made of crude ore.

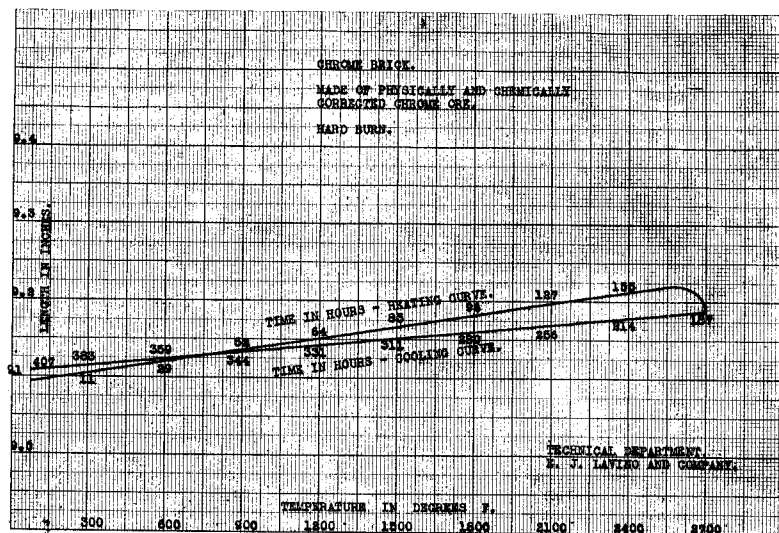**Fig. 14.** Expansion curve—chrome brick made of physically corrected ore. Hard burn.

Fig. 15. Expansion curve—chrome brick made of physically and chemically corrected ore. Hard burn.
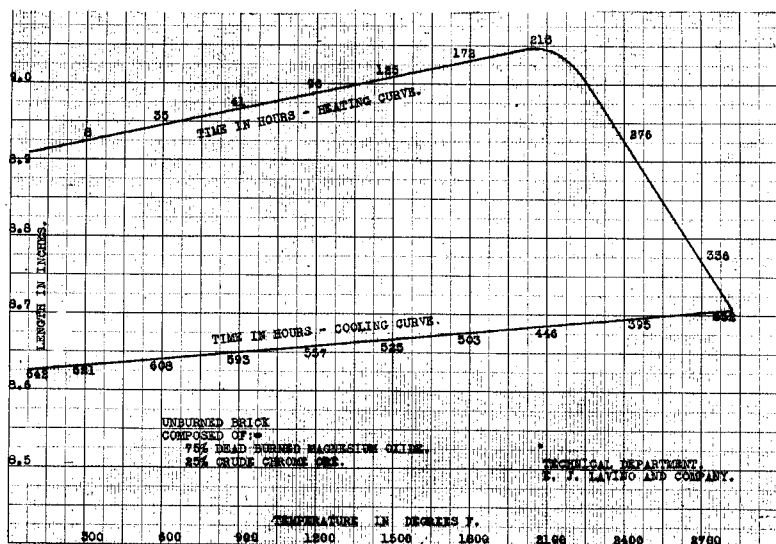

Fig. 16. Expansion curve—unburned brick composed of 75% dead burned magnesium oxide and 25% crude chrome ore.

DISCUSSION

Louis J. Trostel, *Chairman*

C. P. Spangler: (Jones and Laughlin Steel Corp., Pittsburgh, Pa.): What effect has the method of installation on the life of brick? Does gas penetration into the brick effect their life, and is there any relation between installation and gas penetration?

Dr. Seil: This subject has been given a great deal of thought and many experiments have been made in our laboratories to determine exactly what effect the method of installation has on the life of the refractory.

The life of the refractory can be resolved into a series of individual actions. The rate of heat penetration at different points in the individual brick, and at different points in the finished installation is of primary importance and heat penetration is most certainly affected by the method of installation. If the brick is laid dry the isothermal lines in the brick are not parallel with the surface of the furnace wall, but in every brick the isothermal lines are curved, and are closest to the exposed face of the wall at the center of the exposed face of the brick curving away from the exposed face of the brick toward the unexposed faces. Inasmuch as the coefficient of expansion in refractories is approximately uniform, this heat penetration influences the movement of the brick so that the edges of the exposed surface tend to move into the furnace to a greater extent than does the center of the brick. This movement is a primary cause of spalling, which we consider to be a function of the coefficient of expansion and the thermal conductivity. As the thermal conductivity increases the slope of the curvature of the isothermal lines decreases and the tendency toward spalling decreases.

This thought can be followed easily and accounts for losses due to thermal shock (spalling). If the brick are properly installed, with sufficient cement between them, the isothermal lines in each brick are almost parallel to the exposed surface. These isothermal lines are more nearly parallel if the physical properties of the cement used approach those of the brick.

To a certain extent gas penetration follows the same lines. However, the porosity of the brick as a unit and the porosity of the wall as a unit are considerably different. Analyzing the two units we find that if a brick is properly installed with cement the gas penetration can only take place from the exposed surface of the brick. If, on the other hand, the brick is laid dry, the gas penetration can take place from five faces of the brick. In considering the wall or the entire installation as a unit, the porosity of the individual brick, the type of pore, the size of pore, and the thickness of the pore wall are most important factors.

Much more important than the porosity of the individual piece from which the wall is built is the spaces between the bricks when the bricks are laid dry. Incidentally a dry wall is the cause of inward and out-

ward leakage in a furnace and decreases the furnace efficiency to an extent that is almost unbelievable, unless the furnace is operated at approximately zero pressure. The effect of a dry wall on inward and outward leakage, of course, depends on the furnace pressure.

The porosity, which controls gas penetration, also causes other difficulties with brick installations, particularly in respect to slag penetration. Gas penetration, of course, does not affect the brick unless its composition is such that there is chemical reaction. This, however, is not true of slag. When slag penetrates a brick, whether it reacts with the primary or the secondary component of the brick or whether it re mains in its original form, it still changes the physical characteristics of the brick. In most cases there is a very definite chemical reaction between the secondary component in the brick, which is its bond, and the slag. This slag penetration must be considered just as heat penetration was considered. If the slag penetration follows a plane parallel to the exposed surface of the brick it has much less effect upon the brick than if it followed the curved lines explained above.

. This discussion so far gives you the result of many of our experiments. I do not believe it out of place to describe to you a few of the experiments from which we arrived at these conclusions.

We were first interested in finding what type of mineral matter was carried by the gases in an open hearth furnace. In the usual furnace with a silica roof and silica end walls it is almost impossible to determine what the gases carry. However, we had the opportunity of watching a furnace with Kromag end walls, front wall, and back wall with which the mineral matter in the furnace atmosphere did not react. The material which accumulated on the end walls contained 85 per cent of FeO with a little silica and small percentages of lime and dolomite. Inasmuch as the chrome brick which we are discussing are used almost entirely in open hearth furnaces this was an important fact to us. We ran a series of tests to determine the effect of grain size and tempering on the physical properties of the finished brick, particularly in respect to slag penetration. Our first study showed us that the usual method of preparing bricks was not as constant, uniform, and accurate as it ought to be. When a definite grain sizing was prepared and tempered in the wet pan, it was found that the time the material was in the wet pan with heavy mullers influenced the -200 mesh material to such an extent that the physical properties of the brick were greatly changed. A variation from 18 to 26 per cent of -200 mesh material is not uncommon where tempering is done with heavy mullers. This variation in the 200 mesh material effects the porosity by changing the distribution of the pores, the number of pores, the sizes of the pores, the shape of the pores, and the thickness of the pore wall. The change in porosity, of course, has an effect upon the spalling, gas and slag penetration, and other physical properties, such as resistance to deformation due to temperature under load, to sagging, and its heat characteristics.

We next determined by experiment the effect of various materials in the furnace atmosphere on bricks made from the same material but with

different grinds, and in another experiment we determined the effect of varying the bond but keeping the grain sizing constant. We determined the effect of these same materials in the atmosphere on the same brick laid in the proper cement and laid dry. The results of these experiments are best shown by lantern slides which fortunately I have with me. You will note that the furnace in which these bricks were built is in the shape of a hollow square with four burners so arranged that the flames swirl one into the other to give as nearly uniform effect on the various brick as we have been able to obtain. You will note that there are twelve (12) different brick being tested, two (2) of each kind. One set of twenty-seven (27) bricks is laid dry and one set of twenty-seven (27) bricks is laid with the proper kind of cement. They are laid nine (9) high so that we can choose for our samples bricks which are surrounded completely by their own kind. You will note that there are 648 brick in this test of which 216 can be examined for the effect of the furnace. These pictures show quite distinctly that the brick properly laid up in cement resist slag penetration and for that reason spalled much less than the brick laid up dry. You will also note that the grind of the brick has a great effect upon the slag penetration and spalling.

In closing I wish to emphasize the method of using the proper cement between refractories. The function of the cement is to overcome any surface inequalities in the brick so that a surface to surface contact is obtained. For this reason it is necessary to use the minimum amount of cement which will fill all the spaces between the brick, which would not normally come in contact if the brick were laid dry. This entails either dipping the brick in a mortar of the proper consistency, or buttering the joints with a trowel. The consistency of the cement and its plasticity is most important. A cement which is not plastic cannot take care of the inequalities in the surfaces of the bricks. Brick cemented with a dipper are almost useless. If the cement is thin enough to flow into the vertical joints, it is also thin enough to flow out of these joints. The dipper method of laying brick gives a fair horizontal joint but a use less vertical joint. A practical example of this dipper type of installation was personally inspected in one of the large steel companies. A metal mixer which was not operating at full capacity had its brick installed by this dipper method. Because of the curtailed capacity of the metal mixer it was necessary to use oil burners for long periods of time to keep the metal molten. This caused the brick work above the metal line to become hotter than usual. On tilting, the molten metal penetrated into the vertical joints above the metal line, and was oxidized to iron oxide. The iron oxide then reacted with the clay brick and cut vertical crevices in the wall of the furnace to such an extent that in some places they were 15 inches deep. The same furnace laid up with brick with their proper cement with tight horizontal and vertical joints will outlast this dipper method of brick laying at least ten times.

Notes on the Effect of Heat Treatment Upon Spalling of Clay Refractories

BY S. M. PHELPS

Senior Industrial Fellow, American Refractories Institute Fellowship, Mellon Institute, Pittsburgh, Pa.

THE SPALLING of refractories in service has long been recognized as a major cause of failure, and consequently the subject has received much study. It is only in recent years, however, that spalling has been considered as being associated with the permanent changes that are caused by the heat treatment of service. Nearly all of the spalling tests in the past were devised so as to break the brick by rapid thermal fluctuations, ignoring the fundamental changes that are caused by service. The changes that occur in the heated layer of brick in a furnace wall are largely responsible for the spalling which may take place. It is almost impossible to spall, by thermal changes, a new clay brick furnace wall. Unfortunately, it is impracticable to maintain such resistance during the life of the refractory because of the effects of long periods of heating and the contamination by slags.

The primary cause of all thermal spalling is the fact that refractories expand when heated. If thermal expansion were not a property of refractories, spalling could not take place. When a brick is heated on only one side, the heated layer expands and the increase in size of the layer depends upon its temperature and its coefficient of thermal expansion. The important point is, whether or not the properties of the brick are such as to allow the expanded portion to be still a part of the remaining or unheated portion of the brick. If there is sufficient "give" in the structure, the expanded portion will not separate or spall. Because thermal expansion is always a factor, the degree of "give" that the brick possess is highly important. The word "give"* is used here to include the properties of elasticity and plastic flow.

Properties other than these involved in spalling are thermal conductivity and tensile and compressive strength. The rate of heat flow cannot be materially altered in clay brick, and probably not to a degree that would make this factor worth considering. It would seem that the strength of any type of clay brick would not be of a sufficiently high order to prevent thermal expansion from taking place, and consequently it will not be discussed.

Investigators have attempted to formulate the various properties that cause spalling so as to be able to predict spalling behavior in service, and for the purpose of having a better insight of the importance of each factor. In order to evaluate the practicability of any theoretical spalling formula, it is, of course, necessary to have some means of measuring

---

*Dr. W. A. Hamor has suggested in place of "give" the descriptive word "rhelasticity" (from rheo--to flow, and elasticity).

spalling itself.   The use of tests involving the water dip method, either on brick as received or after reheating throughout or on end, is of questionable value.   It is believed, however, that with the development of the panel spalling test a more adequate means of evaluating spalling is available.*   Correlation of the panel spalling test data secured on 40 brands of clay brick representing all of the various types, with their behavior in certain types of furnaces shows a surprisingly close agreement.

The principle of this spalling method is to test a section of a furnace wall rather than individual brick.   The fourteen test brick are laid up so as to expose for treatment the 2½ x 9-inch face, and to form a panel 18 inches square.   The test surface of the panel is heated to 1600°C for a period of 24 hours, during which time the back of the panel is insulated so as to maintain a temperature of 1250°C on the cool side of the brick. The object of this pre-heating is to simulate the results of long periods of time at lower temperatures encountered in industrial furnace operations.

This treatment produces a vitrified layer along the heated face of the brick that varies both in depth and degree of vitrification, depending upon the nature of the brick.   Occasionally brick show in this part of the test a very pronounced expansion or contraction which is sufficient to cause the altered layer to separate or peel from the remainder of the brick.   This behavior has been termed structural spalling, so as to differentiate it from the spalling caused by rapid thermal changes.

The thermal spalling part of the test is conducted by placing the panel in the doorway of a furnace maintained at 1400°C for a period of 10 minutes, and then removing it to a position to receive a blast of air. After cooling for 10 minutes, the panel is heated again, and 12 complete cycles constitute the spalling operation.   The percentage loss in weight resulting from the treatment is used as the index to spalling resistance for a given class of service.   Figure 1 presents the complete panel spalling equipment, showing the furnace for pre-heating and the spalling furnace with the cooling apparatus.

The comments given are interpretations of the behavior of a large variety of clay brick in the panel spalling test.   Remarks will be limited primarily to the properties of reversible expansion and the rhelasticity of the structure, because these factors may be controlled to a degree by manufacturers who profit by an understanding of their importance.

During the development of the panel spalling test, there was conducted a special spalling test on a general purpose clay brick, which is of particular interest here.   In this test, the panel was not pre-heated before the spalling operation and it was found that it would require a treatment in the order of a hundred or more cycles to produce an appreciable loss.   The same kind of brick in the regular test would lose 15 per cent to 20 per cent with 12 cycles, which demonstrates the pronounced effect of the heat treatment on the surface of the brick.

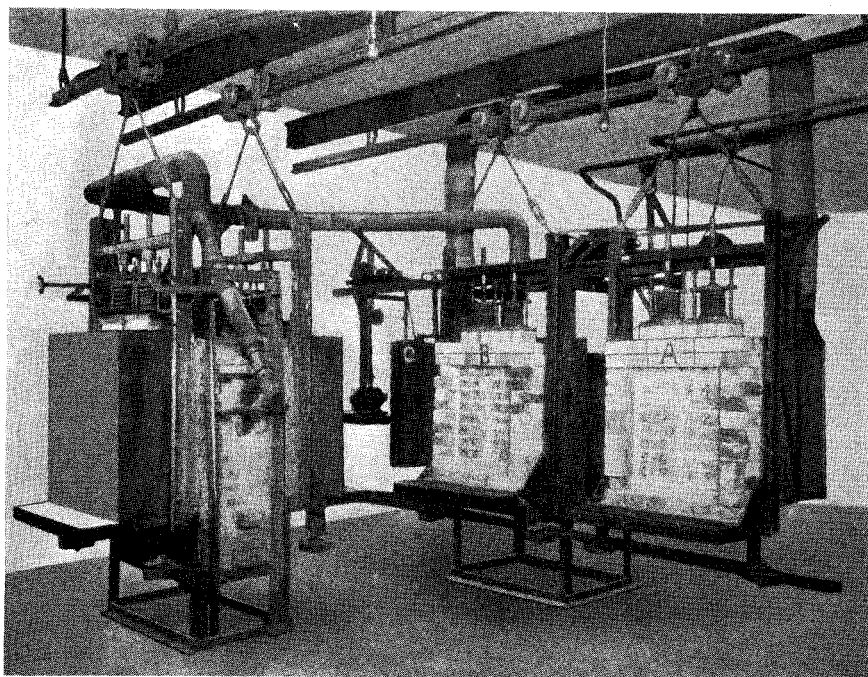* J.Am.Cer.Soc., 14, No. 5.   (May, 1931).

Fig. 1. Complete service spalling equipment. Preheating furnace on the left; spalling furnace on the right with panels in position.

The question is, how has the heat treatment affected the brick? Why is it more sensitive now to rapid thermal changes? The visual effect of the preheating is, in most cases, the production of a vitrified layer which may vary from ½ inch to 1½ inches in thickness. The gradation from this vitrified layer to the normal structure varies in thickness, and this is also dependent upon the nature of the refractory. It seldom happens that the layer which has been vitrified is of the same dimensions as it showed originally. Consequently stresses are produced and subsequent thermal changes may easily increase these to the point of relieving the strains, which results in spalling. Obviously, the greater the volume change caused by heat treatment, the more critical this situation will be. These conditions are permanent and should not be confused with the reversible volume change produced by heating or cooling the brick during spalling, with its resulting effects. The ideal brick from this standpoint would be one in which the heat treatment would not produce an appreciable permanent volume change so that no stresses could be produced.

The question naturally arises as to what change has taken place in the vitrified portion with respect to the temporary thermal expansion. Mr. Heindl's work at the Bureau of Standards[1] has demonstrated that the

[1] "The Thermal Expansion of Refractories to 1800°C", Bureau of Standards Research Paper 562, June, 1933.

expansion may be either increased or decreased by refiring clay refractories to high temperatures. Furthermore, his work on kaolins[2] reveals the fact that the pronounced increase in expansion between 100° and 200°C., which is probably caused by the presence of cristobalite, can be reduced by the addition of a flux that dissolves this silica when the kaolin is refired. Thus the solution of silica by means of high temperatures and fluxes would, in many instances, lower the expansion of the vitrified portion as compared with the remainder of the brick.
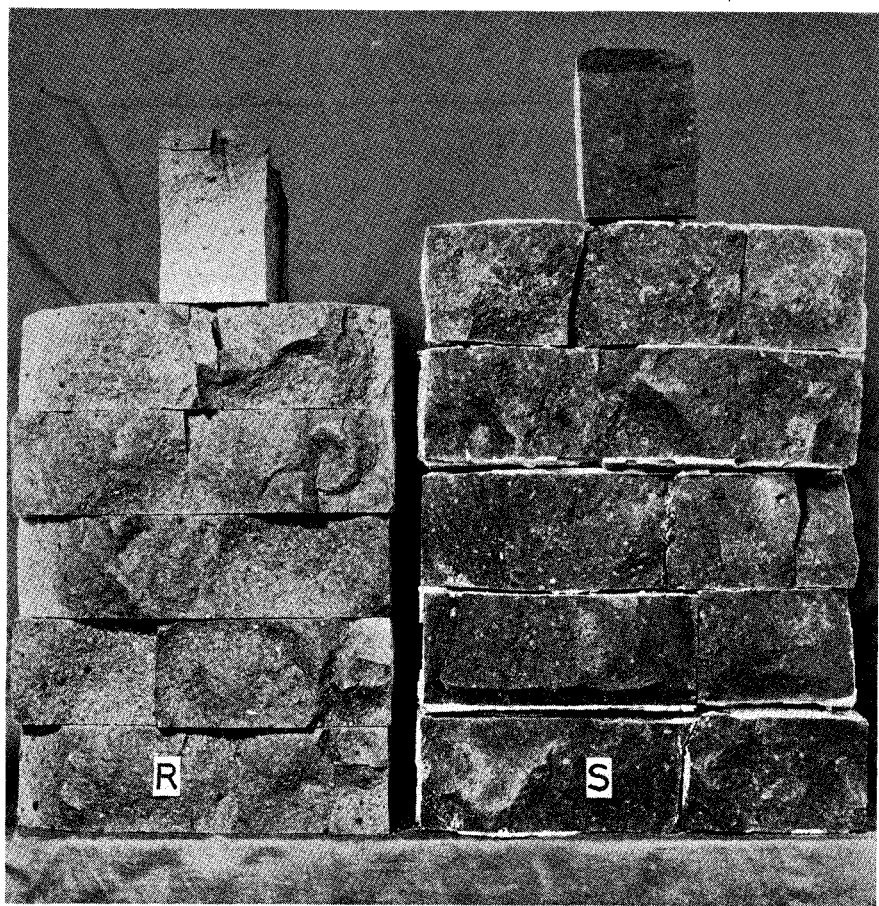
Fig. 2. The appearance of Brand A after both the regular and the special panel spalling tests. The brick labelled "R" were in the regular test and showed a loss of 19.6%. Those labelled "S" had been given prior to spalling a re-heating test at 1600°C for a period of 24 hours. After having been made up into a panel, they were subjected to a spalling treatment only and showed a loss of 26.2%.

[2] "Kaolins, Effect of Firing Temperature on Some of Their Physical Properties", Bureau of Standards Research Paper 410, February, 1932.

Experiments in the panel spalling test have been conducted to demonstrate this feature with a typical stiff mud clay refractory which will be designated as Brand A. These brick show a loss of 19.6 per cent in the regular panel spalling test and have a P.C.E. of 32. Six brick were reheated throughout for a period of 24 hours at 1600°C., so as to have the whole brick of the same structure as the vitrified portion of those that were in the panel pre-heating test. Such heat treatment is, of course, extremely severe, and the brick expanded 14.4 per cent, together with the development of a glassy structure. These brick were laid up so as to form a regular panel and were given the spalling part of the panel spalling test. The amount lost by this treatment was 26.2 per cent, or an increase of 6.6 per cent over the regular test. The appearance of Brand A after both methods of treatment is presented in' Figure 2. This increase in spalling cannot be attributed to the difference in structure between the vitrified portion and the remainder of the brick, but may be explained by thermal expansion or rhelasticity.

There was also included in the reheat firing a suitable sample of brick ''A'' which could be used for a reversible thermal expansion determination. The expansion data obtained from this sample are presented in Figure 3, together with the data from an unheated sample cut from the same brick. These data show an appreciably lower expansion for the reheated sample, along with the elimination of the cristobalite jump. It may be assumed, then, that the increased spalling is not due to a more pronounced thermal volume change, but may be accounted for by the lowered rhelasticity within the brick.
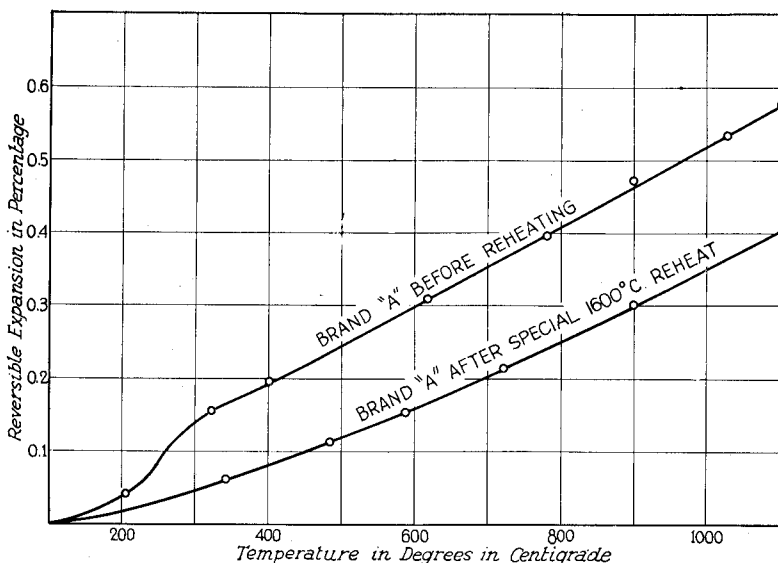

Fig. 3. Graph presenting the reversible thermal expansion of Brand A before and after the special 1600°C reheat.

There is little doubt as to the importance of the properties that are covered by the term rhelasticity, not only as a result of experimentation but also through reasoning.

It is not a simple matter to incorporate in a refractory, together with other properties, a high degree of flexibility.   This is especially true when the effects of vitrification are considered.   A good example of flexibility is present in certain types of insulating brick that are comprised of cellular structure.   These brick are very resistant to thermal spalling because of the flexibility which results from the thin walls about the cells.   There has recently been placed on the market a light-weight refractory which is essentially a silica brick, except that it is extremely porous, with consequent flexibility.   Silica brick are notorious for their poor spalling resistance, but this product possesses exceptional non-spalling properties.

Cellular or porous brick would not be practical in service, so another means of securing this property is necessary.   If the cells or pores could be filled in such a way that the filler would not be in actual contact with the walls, thereby maintaining the flexibility, the problem would approach solution.   Such a structure is in a measure obtained when the proper amount and the necessary proportion of particle sizes of flint clay are incorporated in a clay refractory.   The close fitting grains of flint clay, surrounded with a minimum amount of plastic clay, simulates the structure of the flexible insulating brick.   The flint clay particles should not be tightly bonded together by the plastic, otherwise the rhelasticity would be lost.
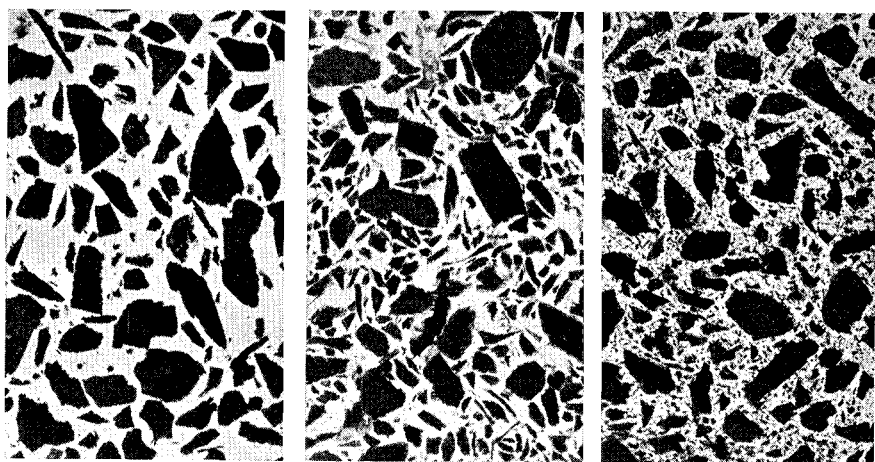
A   B   C

Fig. 4.   Cross sections of three mixes of particle sizes.   The black grains are charcoal particles and are bonded by means of plaster of Paris.   "A" represents particle sizes between 4 and 12 mesh; "B" 50% of 4-12 mesh and 50% 12-20 mesh material; "C" 45% 4-12 mesh, 10% 12-20 mesh, and 45% 20-100 mesh.   (Mag. 4 X).

Figure 4 is a representation of the effects of proportioning particle sizes. The materials used were grains of charcoal bonded with plaster of Paris. After the prepared mixtures had set, a section was prepared by abrading away the surface with sandpaper. The photographs of three types of mixes show clearly the possibilities of developing the proper structure. In recent years the study and practical application of grain size proportioning has led to the development of superior refractories, particularly with reference to spalling. An example of such products is given in Figure 5, which shows the polished section of a brick in which the grain size is well adjusted. There is also shown a section of the same brick after it had been heated for five hours at 1600°C., and it will be seen that the character of the brick is maintained to an exceptional degree.
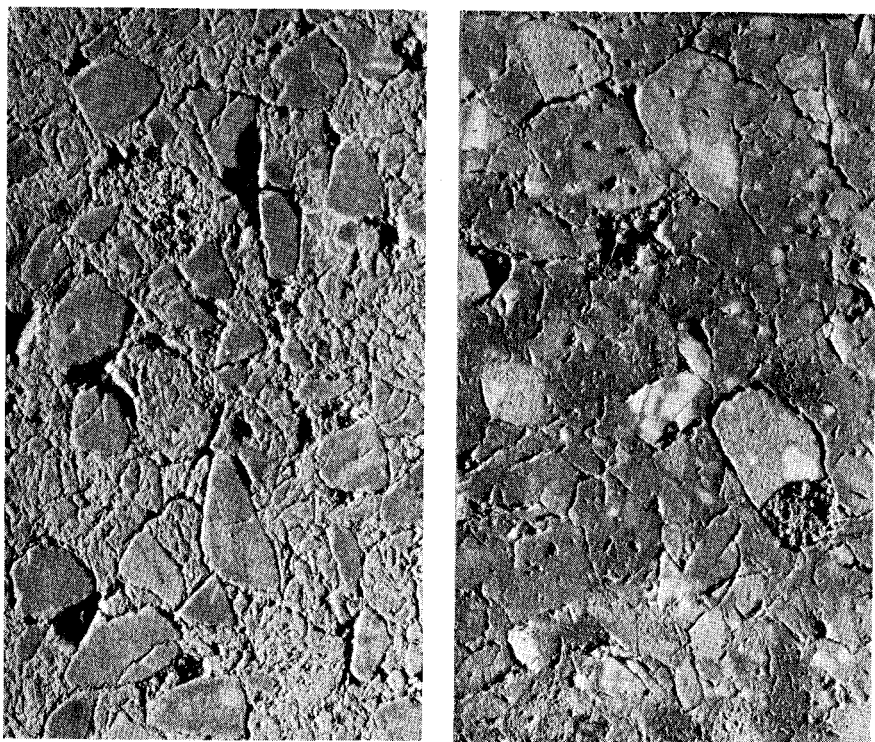
Fig. 5. Photograph of polished section of a non-spalling type of clay brick. The section on the left is the brick without having been heated, while the one on the right shows a section of the same brick after having been heated to 1600°C for five hours.

For the purpose of demonstrating the merit of this type of structure, there were conducted on a spalling-resistant type of brick, which will be designated as Brand B, the same tests as outlined for Brand A. This brick has a P.C.E. of 32-33 and shows in the regular panel spalling

test a loss of 7.1 per cent. In the 24-hour reheat at 1600°C., in which the brick were heated throughout, they expanded 5.0 per cent. After subjecting them to the thermal spalling part of the test, the loss was found to be 3.3 per cent, or less than half the loss in the regular test. The appearances of Brand B after both the regular and the special tests are presented in Figure 6.
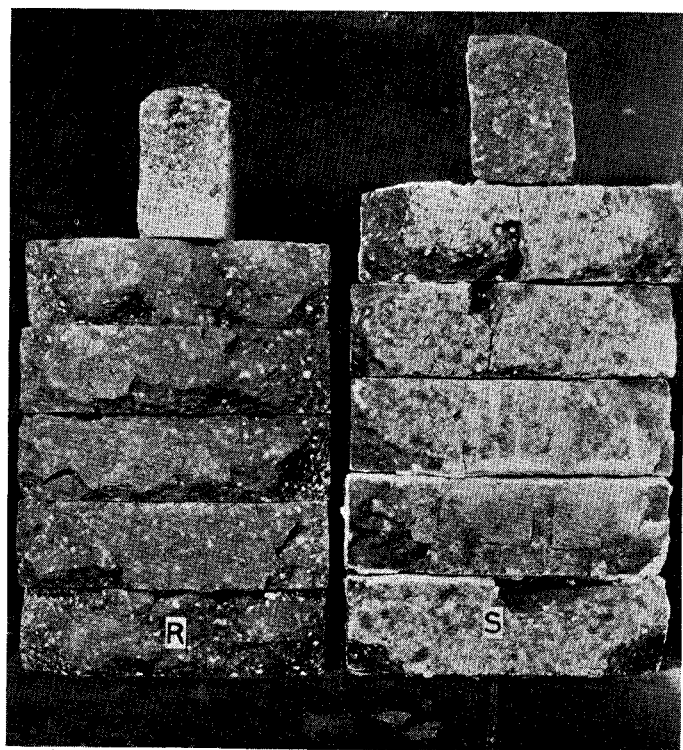

Fig. 6.   The brick of Brand B after having been subjected to the regular (R) and special (S) spalling tests. The losses were 7.1% and 3.3% respectively.

The superior behavior of the brick from the special reheating test may be explained partly by the fact that the rhelasticity within the brick had not been materially reduced, as had been the case with Brand A. The comparison of broken sections of Brand A and B is shown in Figure 7; and although photographic reproductions do not do justice, it should be clear that the structure of A is less desirable than that of B.

The results of testing Brand B also illustrates the effect of stresses, as has been mentioned. Upon reheating the whole brick, the structure may be free of stresses, while this can hardly be expected in the case of the brick heated on one face only. As a result, a smaller amount of
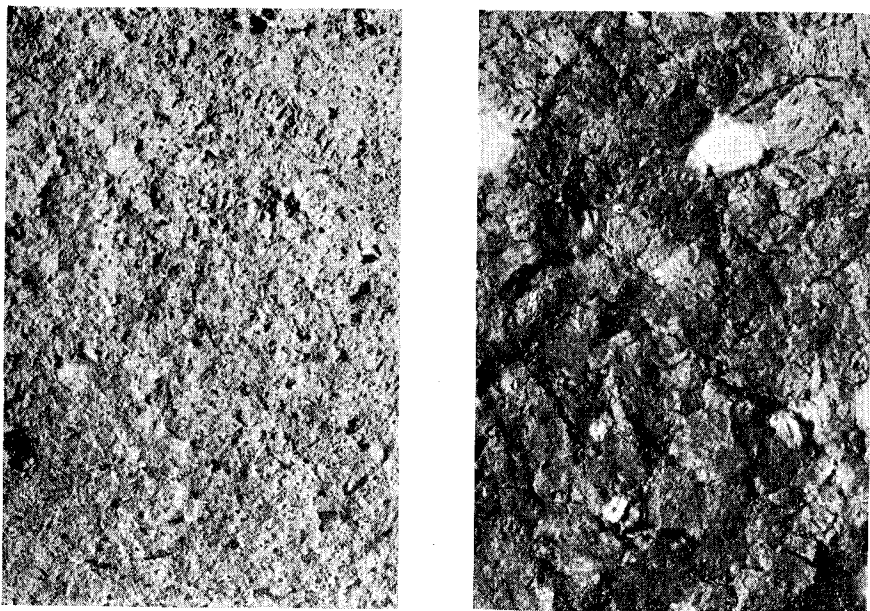
Fig. 7. Photographs of broken sections of Brands A and B. (Magnification 2X).

spalling has taken place in the brick that is free from stress, especially since the rhelasticity has not been impaired.

The isolation and evaluation of the function of stress and rhelasticity can be obtained only by a most careful and thorough study.

An additional factor pertaining to the general subject of spalling is the way in which the spalling fractures develop. This is illustrated by the two brick shown in Figure 8, one of which shows an expansive fracture that is quite characteristic of brick that spall readily. The second brick shows a characteristic of the more resistant type, and this resistance may in part be accounted for by the fracture which produces interlocking fragments. Most of the best types of non-spalling brick develop fine cracks on the treated face, penetrating the brick in all directions, with the result that the surface is an interlocking mass of vitrified pieces. Such a structure possesses in a sense a high degree of rhelasticity, and consequently is very resistant to thermal spalling. This property is in reality distinctly different from the factors that have been discussed, but its importance can be readily appreciated.

The comments given and the experimental work reported, together with the nature of the panel spalling test, show that there is an excellent opportunity for a fundamental study to define the causes of spalling when it is associated with refractories that have been previously heat-treated on the spalled surface. Heretofore, studies on the causes of spalling have had to do mainly with structures that have had a uniform

**Fig. 8.   The spalled face of two distinct types of clay brick.   Note the differ-
ence in fracture between these, the upper one being typical of brick which
spall readily, while the lower one represents the more non-spalling type.**

heat treatment; consequently, the findings are not applicable to spalling
that ordinarily takes place in the industrial furnace linings.

Summary

The factors involved in the spalling of refractories in active service
have been discussed, with particular emphasis being laid on the fol-
lowing points:

   (1)   The set-up of stresses within the brick as a result of
        vitrifying one face of the refractory previous to spalling.

   (2)   The changes in reversible thermal expansion caused by
        heat treatment of the face.

   (3)   The effect of heat treatment or vitrification on the rhelas-
        ticity within the brick structure.

   (4)   Cracking of the face of the brick in a manner so as to
        form an interlocking of the structure of adhering par-
        ticles.

Progress in Heat Treatment of Alloys Resulting from Structure Studies

By David F. McFarland

Professor of Metallurgy and Head Department of Metallurgy, The Pennsylvania State College

METALLURGY like ceramics had its beginnings in the dawn of history and knowledge of the methods of extraction and utilization of metals was but slowly acquired and was handed down from generation to generation as an art or craft. Realization that certain kinds of heat treatments were beneficial to some of the metals in adapting them to use came fairly early but all such treatments were gradually, and more or less accidentally developed. Their details were transmitted as carefully guarded secrets to the chosen few craftsmen who were deemed worthy to carry them on.

Some of these procedures for heat treatment were of the most fantastic, and from our point of view, absurd nature and involved careful attention to details which were later found to be entirely irrelevant, while other really important factors were entirely ignored. They show that not the slightest conception existed of the general principles and fundamental factors underlying these treatments. Heat treatment was an art and not a science. Before scientific heat treatment could develop it was necessary that the sciences of physics and chemistry take form, and that the child of the union of these parent sciences—physical chemistry—be born.

The introduction of metallography—the microscopic examination of polished and etched sections of metals by Sorby in 1864, followed by similar work by Martens, beginning in 1878, Osmond in 1885, Howe and Sauveur in America gave increasing appreciation of the effect of structure of metals upon their properties.

Application of the new principles of physical chemistry to the study of constitution of alloys really began with the work of Matthiessen in 1863. He showed the relation of properties such as density, electrical conductivity and thermo-electric power to alloy composition and sought to relate discontinuities in these properties to the presence of intermetallic compounds.

Studies of the relation of composition to the freezing points of the succeeding members of a series of binary alloys and with various pairs of metals, were published by Heycock and Neville in 1889 and were accompanied in the same year by papers by Ramsey on vapor pressures of alloys and by Tamman on the depression of freezing points produced by alloying. The complete recital of the important steps in development of scientific heat treatment would be too long for the limits of this paper and only a few high points may be discussed which helped to

an understanding of the close relationship of all physical properties of metals and alloys to their structural composition, and the dependence of the latter upon methods of fabrication and heat treatment.

Equilibrium Diagrams

Application of Willard Gibb's phase rule to alloys was suggested by Von Juptner in 1899 and by Le Chatelier in 1900 and Roozeboom, who had in 1899 developed from theoretical considerations the possible types of equilibrium in binary systems, made specific application of the method to the construction of a complete iron-carbon equilibrium diagram (Fig. 2[a]). He used in this construction the results of thermal examinations of iron and steel made by Roberts-Austen and already embodied in a partial diagram, (Fig. 1[b]). He also used the idea of various allotropic modifications of iron, stable in different ranges of temperature, as previously proposed by Osmond (1887 to 1890).
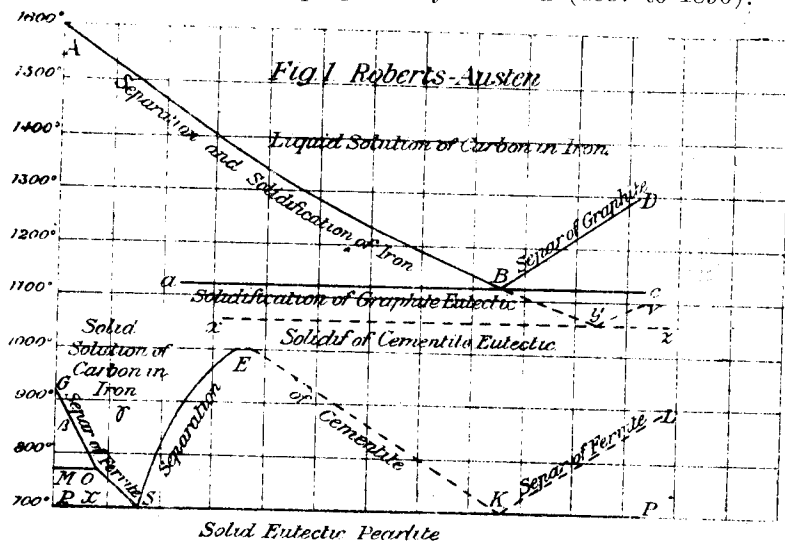
Fig. 1. Iron-carbon diagram according to Roberts-Austen.

This iron-carbon diagram constitutes the most important generalization relating to iron and steel. It has been the focus of countless investigations by later workers and, while it has had to undergo much modification through the results of more detailed experimental work, using improved technique, it has been more productive of practical improvement in heat treatment of metals than any other single factor. A recent form of the diagram is shown in Fig. 3[c].

With the iron-carbon system as example, there has been steady progress in the knowledge of equilibrium relations in all kinds of alloy systems and investigation has been extended from binary systems to ternary and other poly-component systems.

(a) and (b) Jour. Iron & Steel Inst. 1900 (II) pp. 320.
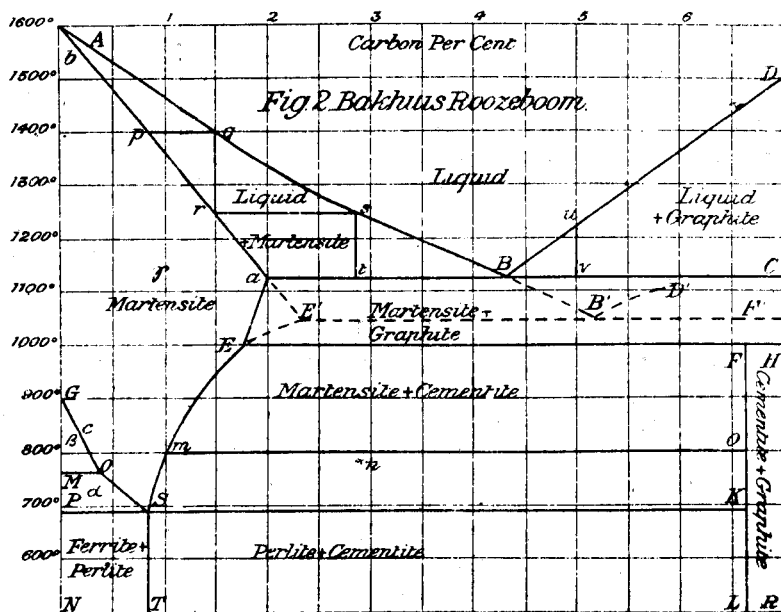(c) Metal Progress. 1930.

Fig. 2. Iron-carbon diagram according to B. Roozeboom.

The Equilibrium Diagram of Iron and Iron Carbide
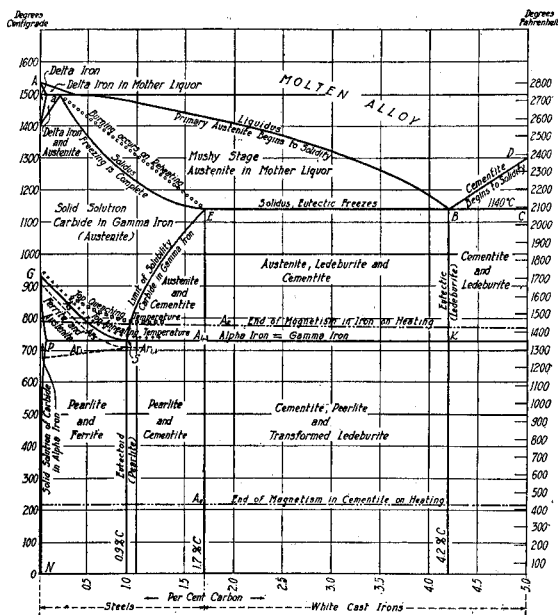

Fig. 3. The equilibrium diagram of iron and iron carbide.

Physical Metallurgy

By correlating the results of thermal and chemical analysis; physical and other test data; microscopic and x-ray spectrographic studies with observations on the effects of hot and cold work, grain size control and forming qualities, it has become possible to establish close control of properties of all kinds of alloy material and to produce any desired quantity of material exactly adapted to a given use. The body of metallurgical knowledge relating to these various factors is now generally called Physical Metallurgy.

Alloys

. Alloys are mixtures of metals in which the component metals may be . mutually dissolved forming solid solutions; chemically combined in intermetallic compounds, or more or less completely separated in a fine grained structure known as an eutectic.

Commercial metals are seldom free from impurities. It is indeed exceedingly difficult to make them even *nearly* pure, and just to the extent that they contain other metals as impurities they are really alloys. This makes alloys our chief interest in the study of common metals.

Crystalline Structure

All metals are predominently crystalline, all the time, although much speculation and attempted explanation of their behavior is based upon the supposed existence of amorphous or non crystalline material at the grain boundaries and on worked surfaces.

The metal crystals are built up of individual atoms arranged in an orderly geometrical pattern known as the space lattice. The size, uniformity, and relative homogeneity of the crystals or grains largely determine the strength, ductility, hardness, and other valuable properties. In general, small and uniform crystals make a strong structure while large uniform crystals make for weakness.

Cast metals, slowly cooled from the molten state usually fall into latter class and are strengthened naturally by having their coarse structure broken up by severe working. The fragments resulting rebuild into a more uniform aggregate of small sized crystals.

Deformation of metals under severe applied stresses takes place by the gliding or slipping of blocks of atoms within the individual crystals over other blocks, along planes of easy separation which are called "slip planes."

Anything which favors easy slipping of these blocks promotes the easy working and relative softness of the metal; while anything which opposes easy slipping promotes hardness, increased strength, and rigidity, and makes working of the metal more difficult.

Heavy work applied to the metal breaks up and severely distorts the crystal structure but if the working occurs when the metal is at a

temperature above a certain minimum known as the ''recrystallization temperature'' the distorted crystals reform into a new pattern which is usually finer grained and more uniform than the original cast structure.

If the work is applied below the recrystallizing temperature the distorted, strained ''cold worked'' structure remains, carrying with it greatly increased hardness and tensile strength but also carrying increased brittleness.

Reheating or annealing the ''cold worked'' metal at a properly high temperature causes recrystallization to take place with regained ductility but loss of the strain hardness produced by the ''cold work.'' Heating too long, at too high temperature causes the grains to grow abnormally large and weakens the structure.

Forms of Heat Treatment

Heat treatment may take a variety of forms depending upon the nature of the metal or alloy treated, and upon the properties desired in the finished product. Briefly, these are as follows:

(A) Annealing—heating to, and holding in a desired range of temperature, to equalize and refine grain structure, to relieve strains, and to obtain the increased ductility, workability, deep drawing qualities and greater toughness that accompany this type of structure.

(B) Heating to control solution of certain structural components in the metal mass—followed by:

(a) Quenching—very rapid cooling to hold these components in solid solution. This leaves the alloy in a state of only partial equilibrium and it is prevented from reacting toward equilibrium only by the rigidity of the metal structure.

(b) Slower cooling, to permit partial precipitation of the dissolved substance in a degree which will give the best combination of desired properties.

(C) Tempering or Drawing which consists in reheating a previously quenched metal in such a temperature range as will allow the reprecipitation or other change which has been arrested by quenching, to take place to some degree. Reheating allows the atoms, which have been fixed in uncomfortable relationships by sudden cooling to rigidity, freedom to adjust themselves to more stable relationships.

All of the above treatments have long been common with plain carbon steels. Knowledge of the iron-iron carbide relationships afforded by careful study of the iron-carbon equilibrium diagram, along with refinement of procedure made possible by close temperature control through use of gas, oil or electric furnaces and accurate temperature measurement, have all contributed to make heat treatment of steel exact in its results even when very large masses and large quantities are involved.

The microstructure and corresponding physical properties resulting

from a given heating and cooling procedure are well known for all common steels and their heat treatment has been fairly well standarized.

Alloy Steels

The growing use of alloy steels has greatly extended the field of heat treatment. Among the effects of special alloying elements upon carbon steels may be mentioned:

(a) Raising or lowering the temperature ranges of stability for the various structural components of the steel as well as for the various allotropic forms of iron. The critical points marking these ranges in any given steel are correspondingly displaced.

(b) Notable effects upon the grain size of the steel.

(c) Introduction of new elements into the solid solution with resulting alteration of the properties of the solid solution or austenitic steels.

(d) Introduction of mixtures of other carbides with iron carbide, either in solution or in combination as double carbides. These have solubilities in iron differing greatly from that of iron carbide and produce much greater hardness.

Addition of one, two, or more special elements to the iron and carbon of steel produces ternary quarternary and other poly-component systems whose complete equilibria are hard to work out and whose treatment is far from simple.

An enormous amount of research and practical testing has been devoted to them and there has been steady progress in correlation of methods of manufacture and fabrication, physical properties and chemical composition, microstructure and macrostructure, heat treatments and results in use *with* such equilibrium diagrams as have been available. More and more this coordination is making possible the selection and proper utilization of the alloy steel best adapted for any given use.

Age Hardening

A particularly interesting development in heat treatment is the so called phenomenon of "age hardening"—also called "precipitation hardening" and "dispersion hardening." This was first utilized in the high strength aluminum alloys developed by Wilm in Germany in 1903-11 for use in Zeppelin air ship construction but was not explained until 1919 when Merica, Waltenberg and Scott investigated the properties of duralumin, an alloy of composition similar to Zeppelin metal.

The alloy on which they worked contained 4 per cent of copper, 0.5 per cent magnesium, and 0.5 per cent manganese—the remainder being commercial aluminum carrying small amounts of other elements—notably silicon.

When this alloy in rolled or forged condition was heated to about 500°C and quenched in water its hardness and strength were increased

somewhat. When, however, the quenched material was allowed to stand or age at ordinary temperature for several days its hardness and strength steadily increased (See Fig. 4[a]). In other words, spontaneous age hardening took place.
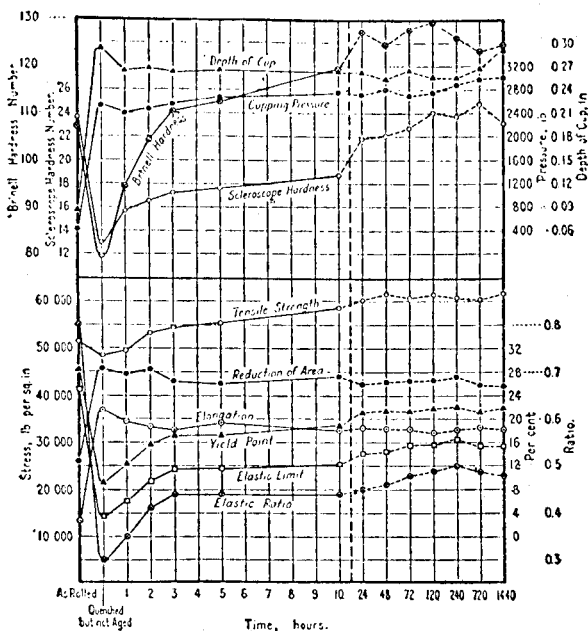

Fig. 4. Spontaneous age hardening phenomena in duralumin: some mechanical properties of No. 18 gauge duralumin sheet as affected by aging to 1 to 1440 hours at the ordinary temperature.

When the freshly quenched alloy was reheated to some intermediate temperature well below the quenching range the same hardening took place quickly, that would otherwise have occurred slowly on allowing the alloy to age. By varying the temperature of quenching and that of reheating considerable variation could be obtained in the amount of hardening produced (See Fig. 5[b]), and the heat treatment afforded a definite control over the "age hardening" phenomena.

The explanation advanced was as interesting as the observed phenomena.—The equilibrium diagram of the copper-aluminum alloy system shows a solid solution of copper in aluminum at the aluminum rich end, and shows that copper is considerably more soluble at 500 to 550° C than is stable at ordinary temperatures (See Figure 6[c]). The excess tends to precipitate out spontaneously from the unstable quenched alloy, not as copper but as copper aluminide ($CuAl_2$) a hard, brittle, inter-metallic compound. Although the particles formed were so small as to not be detectable by the microscope it was thought that their great hardness caused the hardening of the alloy.

(a) U. S. Bu. of Stds. Circular No. 346 p. 251.
(b) U. S. Bu. of Stds. Circular No. 346 p. 250.
(c) U. S. Bu. of Stds. Circular No. 346 p. 235.
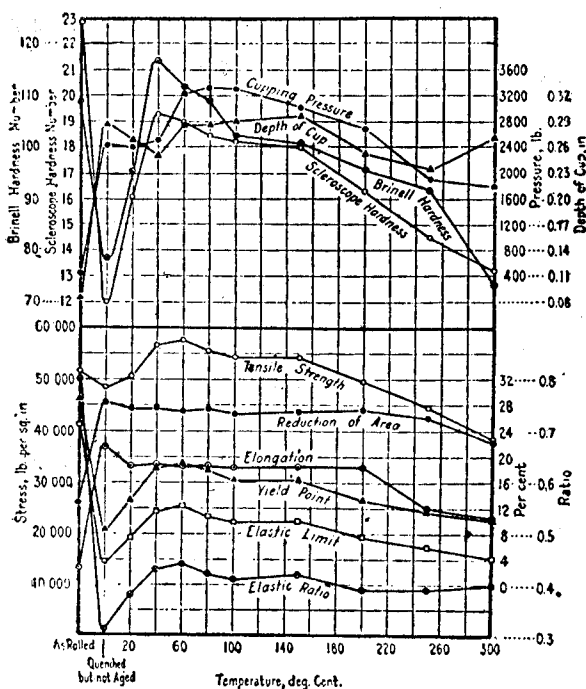
Fig. 5. Controlled age hardening in duralumin. Some mechanical properties of No. 18 gauge duralumin sheet as affected by water quenching from 512°C, followed by aging for 1 hour in the range 20° to 300°C.

Further explanation of this hardening was found in 1921 by Jeffries and Archer in their ingenious slip interference theory of hardening. Applying this to duralumin they postulated that the precipitated particles of copper aluminide did not harden duralumin because they themselves were hard, but because, by being dispersed throughout the crystals of the alloy, they acted as keys between the slip planes of the crystals, preventing their easy slip and therefore opposing permanent deformation. They defined hardness of metals as "resistance to permanent deformation" and called attention to the fact that slip interference would also account for increased tensile strength.

It was assumed that increasing size of the keying particles would cause increased keying power and greater hardness and strength. It was found, however, that after a certain limit was reached the hardness and strength no longer increased. This was interpreted as indicating a critical size of the dispersed particles, or a "critical dispersion" where the precipitated particles would have maximum keying effect and therefore greatest influence for hardness and strength.
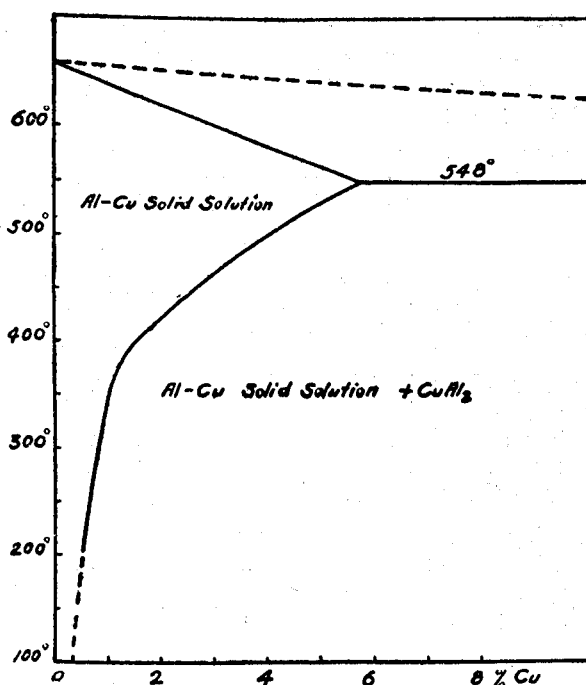
Fig. 6. Aluminum—copper system at aluminum—rich end. (Dix and Richardson.)

TABLE I.—EFFECT OF HEAT TREATMENT UPON 18 GAUGE DURALUMIN (ANDERSON) [a]

Treatment	Proportional limit	Tensile strength	Reduction of area	Elongation in 4 inches
	Lbs/in.²	Lbs/in.²	Per cent	Per cent
As rolled (not treated) _____	40,650	51,740	12.9	2.7
Air cooled from 350° C.[1] _____	7,210	29,900	22.5	11.3
Furnace cooled 350° C.[1] _____	5,080	25,310	39.0	15.0
Air cooled from 400° C.[1] _____	14,080	42,250	24.1	15.4
Air cooled from 500° C.[1] _____	27,770	60,480	24.4	18.5
Furnace cooled from 500° C. _____	7,430	32,290	22.6	15.3
Ice-brine quenched at 512° C.[1] _____	28,620	61,030	26.7	19.6
Oil quenched at 512° C.[1] _____	28,570	61,670	26.3	18.6
Freshly quenched in water at 512° C.[2] _____	14,850	42,280	28.3	21.5
Water quenched at 512° C., drawn 1 hour at 100° C.	20,740	55,250	27.1	18.5
Water quenched at 512° C., drawn 10 hours at 100° C. _____	20,440	55,590	27.7	19.8
Water quenched at 512° C., drawn 1 hour at 200° C.	18,930	49,900	27.3	18.3
Water quenched at 512° C., drawn 1 hour at 300° C.	14,710	38,430	22.1	10.3
Water quenched at 512° C., aged 144 hours in air	28,470	61,170	27.3	17.6
Water quenched at 512° C., aged 1,440 hours in air	28,290	61,650	25.7	18.3

[1] After heating for 30 minutes at the temperature indicated and aged six days at ordinary temperature after the treatment. (144 hours in air.)
[2] Not aged.

This explanation has not only fitted well the observed facts in duralumin but has been found of general application. In other aluminum alloys other compounds such as magnesium silicide Mg_2Si have been

[a] U. S. Bu. of Stds. Circular No. 346 p. 219.

found responsible for age hardening. Control in degree of age hardening is obtained by varying the temperature and duration of the initial (solution) heat treatment and the temperature of the annealing (or precipitation) treatment.

With the striking example afforded by duralumin many other alloy systems which involve varying solid solubility with varying temperatures have been investigated and as a result age hardening has been found and commercially utilized in many systems.

Moreover the hardening and tempering of steel have been explained as a special example of this general phenomenon and further improvements have been made in steel treatment as a result of this explanation.

Many other examples might be cited to show the value of systematic investigation and correlation of all possibly obtainable physical data regarding metals and alloys but enough have been given to explain somewhat the remarkable advances in the use of metals during the past twenty-five years—the era of *Physical Metallurgy.*

Since the analogy between ceramic materials and metals is often very close and since the same fundamental physical laws apply to both fields it may be expected that equally remarkable developments may be brought forth by your continued researches in the field of *Physical Ceramics.*

DISCUSSION

Dr. Frank W. Preston, *Chairman*

Consulting Glass Technologist, Butler, Pennsylvania

Dr. Seil: Dr. McFarland's paper is most interesting and confirms the conclusions which we have reached in our selection of liners for our brick presses. The material from which these liners are made is a high chrome steel containing approximately 12.5 per cent of chromium and 1.5 per cent of carbon with small amounts of other alloy materials. We find that the method of manufacture has a great effect upon the life of the liner. From the same heat we have made three sets of liners. The first were cast with a chill at the wearing surface. This caused all the crystals to be perpendicular to this surface. The rest of the heat was poured into ingot molds which were forged and molded into plates. These plates were fabricated to size, keeping accurate record of the direction of roll. The plate wear was very much affected by whether or not the direction of the brick movement was parallel or perpendicular to the direction of rolling.

Dr. Preston: Mr. Seil's remarks are interesting. We see the same phenomena of slip in the diamond. It is also true of the general behaviour of single crystals. The slip plane apparently has a certain particular angle. The glide planes must be oriented to the direction of slip. In alloy planes similar action must occur. Sorby started the work on crystal structure that metallurgists and ceramists are using at the present time.

Developments and Trends in the Heat Treatment of Electrical Porcelain

By E. H. FRITZ, *Manager,*

Engineering Department, Westinghouse Electric and Manufacturing Company, Derry, Pennsylvania

THE importance of the heat treatment in the manufacture of electrical porcelain has always been recognized from the beginning of the industry, particularly because the ability of electrical porcelain to insulate electrically is so completely dependent upon proper vitrification. To obtain uniform heat distribution in the kilns was therefore, one of the first problems, and with periodic kilns which were, of course, in use in the early days, the solution of this problem was not easy. It was not uncommon in those days to find porous porcelain on a transmission line and many of the outages which were so frequent then could be traced to punctured insulators because of porosity. Today, this condition no longer exists as indicated by outages which are almost unheard of, and the solution of this problem as well as others, both economic and in quality, is evidence of the progress that has been made in the heat treatment or firing of this product. A review of this development will be of interest in connection with this symposium. It is well to state that in this work much assistance was obtained from the investigations and work of others as described in the technical literature. The American Ceramic Society and other technical organizations interested in ceramics have always been actively interested in firing problems and their publications contain much valuable data on this subject.

The kilns which were generally used for electrical porcelain prior to the advent of the tunnel kiln were the updraft direct fire type. A study of this kiln soon showed the possibility for much improvement by better manipulation of the draft. It is at best a very wasteful kiln but it was necessary to at least use it to the best advantage. The type of fuel used dictated largely the details of the changes made but in general they involved re-proportioning the various flue areas and changing the size of the fire boxes, particularly reducing the depth when natural gas was the fuel. CO_2 measurements were taken which indicated excess air as high as 600 per cent throughout most of the burn. High excess air is needed in this type of kiln particularly through the oxidation stage but this seemed excessive after oxidation was complete. This led to the installation of dampers in the top of the bottle shaped stack. These dampers developed full advantage of the changes that had been made in the flues and fire boxes, for the draft could now be controlled at will throughout the burn and uniformly in all parts of the kiln. It was now possible to reduce the draft decidedly after the oxidation period so much so that the top of the kiln chamber was actually under a slight pressure which is favorable for more uniform heat at the top of the kiln setting where much of the porous porcelain had always been found.

From an economic standpoint, these changes were also very beneficial, an average reduction in fuel consumption of 20 per cent resulting.

While this work was going on, attention was also being given to the effect of grain size, particularly of the feldspar, on the firing results. In 1917, an article by Dr. Rieke[1] appeared in ''Sprechsaal'' on this subject. Dr. Rieke corroborated the findings of previous investigators, finding considerably earlier vitrification of all porcelain compositions when finer grain feldspar was used. Feldspar as it was then produced was very coarsely ground and while considerable pressure was placed on the producers, it was not possible to obtain the fineness that seemed necessary. It seemed highly desirable to the electrical porcelain manufacturers to have this fineness to aid in the vitrification of the product and thereby assist in their effort to eliminate porosity. They therefore installed their own grinding equipment which made them independent of the variable and generally coarse grinding of the producers. The results without question justified this step. Vitrification proceeded more rapidly, the firing range of the body was increased, which simplified considerably the problem of obtaining complete vitrification throughout the kiln without overfiring parts of it. It is largely due to the work and results of the electrical porcelain manufacturers that finer and more uniform grinding of both feldspar and flint has been developed by the producers, and while some additional grinding is still done by the manufacturers, the amount has been considerably reduced. Where residues of 20 per cent to 30 per cent on 325 mesh were common formerly, this residue will now run uniformly between 8 and 10 per cent on standard grades.

With the improvement that had thus been brought about in obtaining complete and more uniform vitrification, the elimination of porosity became possible and overfire occurred very rarely. This ended not only the danger of faulty insulators on a transmission line due to porosity but also resulted in improved mechanical and impact strength. It is well established that porcelain reaches its maximum transverse, compressive, and impact strength when minimum porosity is reached. As the temperature is increased and overfiring is approached but before there is any increase in porosity, these values again begin to recede. Sortwell[2] shows this in his investigation of vitreous china bodies which are comparable to electrical porcelain in this respect. This also holds in regard to dielectric strength as shown by Monack, Shardley and Wamsley[3] in some recent work.

The need for improving the thermal shock characteristics of the porcelain introduced another firing cycle problem. Public Utilities in their demand for more dependable and longer life insulators to improve their own service began to insert thermal shock tests in their specifications. These tests involved repeated cycles of immersions in water between

[1] On the influence of size of grain of the aggregate on the behavior of fine ceramic masses during burning, Dr. Reinhold Rieke—Sprechsaal—1917.
[2] The effect of variation in firing on the physical properties of vitreous china bodies, H. Sortwell. Journal American Ceramic Society. 16, 915 (1923).
[3] "The Dielectric Strength of Porcelain—The Influence of Firing Temperature."—Monack, Shardley, and Wamsley—Journal American Ceramic Society, 15, 126-129 (1922).

extremes in temperature as high as boiling and freezing. When one considers that he would not subject his fine tableware to such a test, the severity of this test can be appreciated particularly when it is considered that electrical porcelain designs are comparatively thick and variable in cross section. In the course of the tests that were made, it became apparent that there was a difference in the performance between individual kilns indicating that the firing procedure influenced the ability of the porcelain to pass such tests. A study was therefore made of variations in the firing and cooling cycles, the cooling cycle being considered in this case because it was strongly suggested that the quartz inversion at 575° with its volume changes had considerable to do with this. Furthermore, it had been found that the coefficient of expansion of quartz above and below this point is not the same. Kohl[4] in his very fine paper for instance points out that the expansion of quartz below 575° is regular and high compared to the other constituents of porcelain. The inversion from alpha to beta quartz involves considerable volume change and he shows further that in the beta form above 575° there is no further expansion but slight contraction. The increased importance of the temperature cycle below 575° is therefore apparent. In the study that was made, the heating up cycle was not given much concern inasmuch as the oxidation period, and the elimination of mechanical and chemical water through this stage together keep the rate within safe bounds. On the cooling side, however, considerable attention was directed due to the effect of weather conditions on the rate of cooling of periodic kilns and the lack of any definite procedure in cooling. Tests made on insulators cooled at various rates above and below 575° showed quite definitely the increased brittleness and resulting inferior thermal shock performance of the porcelain if the cooling was rapid from 650° down. Above that point the rate had no apparent effect. On the other hand, with slow cooling below that temperature, satisfactory thermal shock properties were obtained. This led to an established cooling cycle, cooling rapidly in the early stages and slowly below 650°C.

When the tunnel kiln came into use, electrical porcelain manufacturers were quick to recognize its economic advantage and its possibilities for improved firing control because of the continuity of operations and the comparatively small cross section subjected to heat treatment. They were, therefore, among the first to adopt this kiln. The developments in firing procedure with periodic kilns were readily adapted to the tunnel kiln in its design and the control features built into it. A description of these in our case was published in an article several years ago[5]. This covered particularly the continuous maintenance of proper heating and cooling conditions. The work which had been done with the periodic kilns proved to be of great value for the results with the tunnel kiln were immediately highly satisfactory. The advantages which had been expected from it were fully realized, particularly a

---

[4] "The Heat Expansion and some other Physical Properties of Porcelains as a Function of the Composition and the Firing Temperature." Dr. H. Kohl. Berichte d. Deutschen Keramischen Gesellschaft. Dec., 1922.

[5] A Tunnel Kiln Installation for Porcelain Insulators. E. H. Fritz. Journal American Ceramic Society. Nov., 1929.

tremendous fuel saving, and from the standpoint of quality, less variation in the maturing temperature amounting to not more than one cone. This meant that with proper handling of the kiln, there need no longer be any concern over underfired or overfired porcelain.

As production with the tunnel kiln continued and the period of high business activity was entered it became necessary to obtain maximum output from it. The major limitation with faster movement of the cars, seemed to be the difficulty of maintaining proper oxidation of the porcelain for a tendency toward blue coring developed. The condition confined itself to the inner parts of the cars at the bottom, which was to be expected, but CO_2 measurements indicated that the kiln atmosphere was sufficiently high in excess air. This suggested that the temperature cycle·in this part of the cars was not the most favorable for oxidation and it was therefore decided to make a complete investigation of oxidation as it applied to our product. Work was first done in the laboratory on the rate of oxidation of the porcelain body and the individual ball clays. The results of this work have been published[6]. This showed definitely that oxidation proceeds rapidly starting at 250°C, continuing up to 650° and is dependent almost entirely on temperature and very little on time, provided a reasonable firing schedule is followed. These results seemed to make the problem more simple since if a temperature increase of not exceeding 25°C per hour could be maintained through this range over all parts of the car, satisfactory oxidizing conditions should result. Continuous temperature measurements were taken on a car as it passed through the heating up cycle by fastening thermo couples on the ware setting and unwinding the lead wire from a reel as the car moved. Couples were fastened at four points, the top and bottom on the outside and inside respectively. At the same time, in order to get a more definite measurement of blue core conditions, porcelain rods $2\frac{1}{2}$, $3\frac{1}{2}$ and $4\frac{1}{2}$ inches in diameter were fired in the inside bottom of the car where this condition developed. These sizes were chosen because they start with the maximum thickness of commercial designs and go considerably beyond that. The temperature measurements showed considerable lag on the bottom at the start, particularly on the inside, so much so that oxidation did not commence until 22 hours after entering the kiln, while at the top the same point was reached in eight hours. The gap between top and bottom gradually closed as the maturing temperature was approached, which brought about a condition where the bottom inside of the car passed through the latter half of the oxidation range very rapidly. This seemed to be responsible for the blue coring condition and, it was therefore necessary to eliminate or at least reduce the lag in temperature at the bottom so that a more gradual rise in temperature through the oxidation stage would be obtained in this part of the cars. This was accomplished by completely sealing with asbestos rope the opening between the car frames and by lighting additional furnaces which had been idle which increased the volume of combustion gases and improved the gas movement around the individual insulators. This change increased the fuel consumption slightly. The sealing of

[6] The Rate of Oxidation of Porcelain and Ball Clays—Kraner & Fritz, Journal American Ceramic Society, Jan., 1929.

the opening between cars reduced the cooling effect from the comparatively low temperature below the car. Temperature readings after these changes had been made showed that the bottom of the car reached the oxidation stage in 15 hours and the top in seven hours as compared to 22 and eight hours respectively prior to the changes, thereby reducing the temperature lag almost one-half. Attempts to reduce this lag further were unsuccessful and this seemed to be about the best that could be done in view of the natural tendency for the top of the cars to heat first.

The effect of these changes on blue core conditions was definitely improved as indicated by the porcelain rods. Before the changes, the $3\frac{1}{2}$ and $4\frac{1}{2}$ inch rods were blue cored and the $2\frac{1}{2}$-inch rod to a slight extent. After they had been made, the $2\frac{1}{2}$-inch rod was entirely free of blue core, and the $3\frac{1}{2}$-inch rod had only a very slight amount of it. This indicated that commercial designs should be free of this condition entirely which was substantiated by actual results under the faster kiln schedule desired.

The results of this investigation showed the effectiveness of the porcelain rods as a check on oxidation conditions in the kiln and they were therefore adopted as an item of control. These rods are now placed in the kiln at regular intervals so that a continuous periodic check is obtained on oxidation. With slower kiln schedules, this check is of course not important but it is made nevertheless. Desired results are adjusted for the different schedules and in this way a check is at all times available as to whether the kiln is operating under the most favorable oxidation conditions possible. In addition, a recording CO_2 meter has been installed to provide a continuous check on combustion in general. The results with it have also been adjusted for different operating schedules and in this way, this entire problem is now under very close control.

Some further improvement of this general condition has been obtained by the installation of small auxiliary burners where gas is used for fuel. These burners are located mostly ahead of the furnaces at the bottom of the tunnel. By means of these it is possible to maintain the necessary volume of combustion gases for proper oxidation and in addition they make possible the supply of some of the heat units where and when they are particularly needed. The amount of fuel burned at the main furnaces is thereby considerably reduced resulting in a net saving in fuel consumption, and the lag in temperature between bottom and top has been reduced slightly more. These burners are therefore further insurance against improperly oxidized porcelain.

This brings me to our most recent work which has given some rather interesting and unusual results. In connection with a study of the progress of vitrification in the tunnel kiln over the standard firing cycle, porcelain bars $\frac{3}{4}$ inch in diameter by 6 inches long were placed in saggers from which the sides had been broken and loaded on consecutive cars at such a height that the bars could be withdrawn through the middle peep holes between the fire boxes in the hot zone. The bars were drawn from the kiln in this way at various points along the hot

zone starting with a point immediately ahead of the first fire box. Immediately upon drawing the bars from the kiln, they were buried in sand, and allowed to cool in this way. Porosity and modulus of rupture determinations were then made. When a bar of this size is fired completely through the tunnel kiln in the regular way, it will show an average modulus of rupture close to 12,000 pounds per square inch. These draw trial bars gave a modulus of 11,000 pounds when vitrification had just begun and the porosity was still as high as 10 per cent. At the first point of complete vitrification and zero porosity, the bars averaged 14,000 pounds and held that strength through the remaining points in the hot zone. This means with the unusual cooling procedure that was used, an increase in strength close to 20 per cent was obtained over that resulting from the cooling cycle in the tunnel kiln. This cooling procedure involved of course extremely rapid cooling at first, gradually slowing down until comparatively slow cooling was obtained through the critical range of quartz inversion and below, previously described. This difference in strength was so large and was so consistently obtained that it could hardly be ignored. A check was made in a laboratory furnace, following as closely as possible the temperature cycle existing with the draw trials and the results were practically the same. As a further check, the tunnel kiln firing and cooling cycle was then reproduced to a fairly close degree in the laboratory furnace and the strengths dropped to close to the 12,000 pounds average obtained in the tunnel kiln. The effect of the unusual cooling cycle on the modulus of rupture could therefore be accepted as real and was not a freak result.

An analysis of this work indicates to us that the higher strength with the unusual cooling procedure is due either to a structural change in the porcelain or to internal strains. As far as a structural change is concerned, the most likely possibility is that the extremely rapid cooling retards the development of crystal growth. Some of our microscopic work has suggested that the development of a crystalline structure is unfavorable to the strength of the porcelain. Some recent work by the Bureau of Standards, covering the effect of repeated heating on the mechanical strength of insulator porcelain also brings this out. It is shown that after seven heats, long fine mullite needles are present which were not in evidence after one heat. The modulus of rupture after seven heats was from 5 to 35 per cent lower[7]. Since no crystal structure can be seen after one heat, on the basis of the regular firing and cooling cycle, a comparison under the miscroscope of regularly fired porcelain and porcelain cooled in this unusual manner therefore does not disclose anything definite since neither shows any crystal development. However, it is still possible that there is retardation of crystal growth with the rapid cooling since it might well be below the microscopic range. If this should be the cause of the change in strength, it may be possible to reproduce the condition without resorting to the unusual cooling cycle. The idea under consideration is to introduce into the body composition another component which will have the effect of adding an-

---

[7] Effect of Repeated Heatings on the Mechanical Strength of High Tension Insulator Porcelains. Paper by R. F. Geller. Bulletin of American Ceramic Society. 12, 18-25 1933.

other phase to the system thereby eliminating or reducing the tendency toward crystal growth. It has been suggested that the addition of Al_2O_3 might have such an effect. There are undoubtedly other possibilities along this line and it is planned to do some intensive work on this subject.

On the other hand, if internal strains are responsible for the change in strength, the problem is one of heat treatment. In this event it is considerably more difficult due to the limitations that are imposed. All of the shaping of the product must be done prior to any heat treatment and this means that any manipulation of the heat treatment must take into consideration the variations in design and weight of the individual pieces and therefore will be under considerable restraint. In this respect, we are at a severe disadvantage with the glass manufacturer who does his shaping after the maturing temperature of the mix has been passed. However, some approach to the desired cooling condition can undoubtedly be made in commercial kilns possibly involving some change in kiln design, but whether this will be sufficient to gain the desired end, can only be determined by trial.

It seems to us therefore, that here is an excellent field for further work. The fact that a simple change in the cooling cycle produced considerable increase in the strength of the porcelain shows that we have by no means exhausted the possibilities of a feldspar-flint-clay composition, particularly from the standpoint of heat treatment and its effect on the composition. This is emphasized by some recent work by Badger[8] which showed that water vapor accelerates very decidedly the rate of vitrification of bodies containing feldspar, produced by the solution of H_2O in the feldspathic glass. This is extremely interesting and additional work should be done to fully develop the commercial possibilities of this finding. While on first thought, the advantages derived from this would seem to be largely economic, there is a possibility that this action of the feldspar may influence the structure of the porcelain and thus affect its strength in which case the problem would be directly related to the one previously discussed. With the wide application that is made of feldspar-flint-clay bodies, any work on problems of this kind is always of great value, and it is hoped that others will interest themselves in this work. Inasmuch as the work can be carried on almost entirely in a laboratory, it should make a very suitable subject for Government and University Laboratories. With the splendid facilities that are available here and at the other ceramic schools, there is no question that some very valuable work of this kind could be done at the schools and it is offered as an interesting and constructive subject for undergraduate or graduate theses.

[8] Effect of Various Gaseous Atmospheres on the Vitrification of Ceramic Bodies. A. E. Badger. Journal American Ceramic Society, *16*, 107 (1933).

DISCUSSION

Dr. Frank W. Preston, *Chairman*

H. A. Plusch: (Precision Grinding Wheel Company, Philadelphia, Pa.): Was stronger porcelain produced with or without crystals of microscopic size?

Mr. Fritz: Without large crystals. The strength appears to lie in the vitreous phase.

Dr. D. F. McFarland: It is well recognized by students of alloys that increase of grain size leads to a loss in mechanical strength. A single crystal has very low resistance to shearing forces as compared with polycrystalline material.

Mr. Plusch: How about making a low temperature porcelain by using an increased amount of fluxing material?

Mr. Fritz: We have found that high temperature porcelains are the best.

The Influence of Heat Treatment on the Diffusing Properties and Color of Glasses

By H. H. Blau, *Director of Research, and* C. A. Stone, *Chief Physicist, Macbeth-Evans Glass Co., Charleroi, Pa.*

THE COMMERCIAL importance of glass may be attributed largely to its distinctive properties for transmitting electro-magnetic waves. It is well known that glass is quite unusual in having low electrical and thermal conductivities, associated with the relatively high transmissions in and near the visible frequencies. This last property may be determined by the heat treatment to which the glass is subjected, almost to as great an extent as by its composition. These relations may well be illustrated by considering glasses whose light modifying properties are quite specific, that is, colored and light diffusing glasses.

The processes by which such glasses are produced are so largely a matter of heat treatment that it is necessary to limit the scope of the present paper to thermal treatments influencing the transmission of light through the glass with respect to direction and to selective absorption. Most of these heat treatments are effected at temperatures corresponding to relatively great glass viscosities. These processes so involve the time factors of thermal histories of glasses as to recommend a kinetic viewpoint in contrast to the static or equilibrium considerations commonly used in silicate technology.

Before describing the behavior of these glasses during heat treatment, the physical requirements for light diffusing glasses may be briefly reviewed to advantage. Glasses which diffuse light as a result of their internal structures do so because they contain many tiny inclusions of different indices of refraction from those of the surrounding glasses. Thus, light is scattered in the course of its passage through the glass, by encountering one or more of these inclusions, with resulting reflection, refraction, or diffraction. The results of these physical relations afford a suitable basis for the development of the proper physicochemical means for fulfilling these requirements. The diverse approaches of theoretical physics and empirical studies of models of diffusing media have led to the general equations:

$$F_o = F_t + F_s + F_a$$

$$\frac{I_t}{I_o} = 1-(N_q + \mu)t \text{ or } \log_e\left(\frac{I_o}{I_t}\right) = (N_q + \mu)t$$

$$\frac{I_o - I_t}{I_o} = K_s(F_s + F_a) = 1 - 1-(N_q + \mu)t$$

It should be noted that the scattering coefficient, q is proportional to $\left\{\frac{(n_1{}^2 - n_0{}^2)}{(n_1{}^2 + 2n_0{}^2)}\right\}^2 \frac{r^6}{\lambda^k}$ for monochromatic light and suspensions of spherical dielectric particles. This coefficient is so complex that several

of the factors introduced may well be considered independently. In summarizing, these relations show that the diffusion in glasses of the type under consideration is primarily a function of:

(1) The wave length of the light emitted by the source
(2) The thickness of the glass
(3) The absorption coefficient of the glass
(4) The values of the indices of refraction of the inclusions and the glassy matrix
(5) The character of the inclusions
(6) The number of inclusions per unit of volume
(7) The dimensions of the inclusions

The relation of wave length to scattering coefficient may be expressed as:

$$q = K^1/\lambda^k$$

Rayleigh showed that theoretically K may possess a limiting value of 4; but others have shown that it has a value of about 2 for most opal glasses and as low as 0.2 for some alabaster glasses. Obviously, if K is equal to 0, the light scattering becomes independent of the wave length, and this has been approached only in the cases of glasses containing relatively large inclusions.

The absorption coefficient of the glass, μ, is not actually independent of the scattering coefficient, q, although it seems to be primarily a function of the content of the usual glass-coloring impurities or constituents, as well as the distance traversed by the light within the glass. Various workers have estimated that the light actually passes through the equivalent of four to eight times the thickness of opal glasses, but there is not complete accord in their several estimates of the relative absorption of light by the glassy matrix and by the inclusions. The discrepancies in the data may be attributed to such differences between the aqueous suspension models and the actual glasses as adsorption of light-absorbing substances by the inclusions, the character of the inclusions, or the lack of homogeneity of the crystallites. In general, it is even more essential in diffusing glasses than in transparent ones to minimize the contents of such impurities as iron.

That the indices of refraction of the inclusions and of the glassy matrix have a marked influence on the scattering coefficient, q, is shown by the relation:

$$q = K \left\{ \frac{(n_1{}^2 - n_0{}^2)}{(n_1{}^2 + 2n_0{}^2)} \right\}^2$$

It should be emphasized that this relation is subject to rigorous interpretation only when n_1/n_0 is greater than, but approximately equal to, unity. Several workers have reported from their x-ray studies that the inclusions in the commoner fluoride opal glasses are crystallites of calcium and sodium fluorides, the relative amounts of each varying with the particular compositions used.

Agde and Kraus found that only sodium fluoride crystallites were present in the glass even if all of the fluorine was introduced as alum inum fluoride. Gehlhoff, Kalsing, and Thomas, investigated simplified opal glasses containing respectively alumina, zinc oxide, strontium oxide, barium oxide, magnesium oxide, and lead oxide; but were unable to obtain sufficiently well defined x-ray lines to identify the crystallites with any certainty. W. Bussem and W. Weyl employed the same glasses for their investigations and by using the Debye-Scherrer-Hull x-ray method, identified crystobalite and sodium fluoride in all of the glasses. They also observed cristobalite on examining the same glasses under the petrographic microscope. It is probable that the samples were subjected to further heat treatment to obtain better defined x-ray spectrograms; but with the incidental formation of cristobalite. This work is not in agreement with the results of those who have worked with compositions more nearly approaching those of commercial opal glasses and without abnormal heat treatments.

The values of the indices of refraction of the identified crystallites and of typical glasses, in which they may be imbedded, are as follows:

Cristobalite	..............1.487	Soda-lime glass	.............1.52
&	.................1.484	Borosilicate glass	...........1.49
Calcium fluoride	..........1.434	High-lead glass	............1.65
Sodium fluoride	..........1.336		

Calculations using the above data reveal that the scattering coefficients may be varied thirty fold by the extreme combinations of refractive indices. However, these views are entirely on an optical basis, and there are usually other physical, as well as chemical, limitations which tend to restrict the use of this entire range of refractive indices. Moreover, it will be shown that the diffusion of light may be more satisfactorily controlled on the basis of the size of the inclusions and their number per unit volume.

The number of inclusions per unit of volume, N, is a flexible, although limited, means for obtaining the desired illuminating properties. For a given glass it is usually simpler and more precise to refer to the number of inclusions per unit of mass, rather than per unit of volume, when there are extensive temperature ranges such as those in the thermal treatments to be described. The value of N is usually quite high, and for ordinary opals has been determined to be of the order of magnitude of 1×10^{11} to 10^{12} per cc. In general, the greater the number of inclusions, the longer is the average light path through the glass, and, in all actual glasses, the greater is the light absorption. Accordingly, practical considerations limit the extent to which this variable should be employed to obtain light scattering. The influences of the particle number on the general illuminating properties have been thoroughly investigated by Lax, Pirani, and Schonborn.

Both the theoretical and empirical approaches indicate that the size of the inclusions affords the most flexible means of determining internal

diffusion if other factors are properly fixed. The logarithm of the efficiency of the direct transmission decreases as the first power of the particle number, *N*, but it varies as a higher power of the radius of the particles, *r* (according to the Rayleigh equation, as the sixth power). Hampton has derived the following values for the relative scattering power on the basis of the methods suggested by Ryde and Cooper:

PARTICLE DIAMETER	RELATIVE SCATTERING POWER	PARTICLE DIAMETER	RELATIVE SCATTERING POWER
Cm. × 10⁴		*Cm. × 10⁴*	
0.2	1	1.0	1,730
0.5	87	2.0	35,000

He has also shown that the weight of the scattering particles is somewhat less than 4 per cent of the total weight of a typical opal glass. It seems probable that inclusions of diameters somewhat greater than the maximum wave lengths of visible light are most desirable for approaching perfect diffusion with the efficient transmission or reflection of light. The general conclusion of the workers in this field seems to be that the size of the inclusions has a preponderating influence on the diffusion of light and associated properties of glasses.

Spontaneous Formation of Crystallites

It may reasonably be concluded that the number of inclusions per unit of volume, and their dimensions, are important factors in determining the properties of internally diffusing glasses. In the cases of many of these glasses, in which the inclusions are crystallites such as fluorides, means are available for fixing these factors within fairly satisfactory limits. These methods are based on molecular kinetic conceptions of crystallization developed by de Coppet and Tammann. Although direct measurements to substantiate their views were carried out on supercooled organic substances, this hypothesis has been satisfactorily applied to metals and the devitrification of glasses. Indirect measurements have confirmed the view that it may be adapted equally well to many types of opal and certain colored glasses.

The determining factors in the formation of crystallites are the rates of nucleus formation and the velocity of crystallization. Their application to the more widely known types of opal glasses ("spontaneous opals") may be demonstrated by Figure 1, in which the curves represent, respectively, as functions of temperature:

A. Viscosity of the glass

B. Rate of nucleus formation (number of nuclei formed per unit mass of glass per minute)

C. Crystallization velocity (vectorial rate of crystalline growth, microns per minute)

The process of cooling and the attendant development of diffusing properties may be briefly outlined as follows from Figure 1: The opal
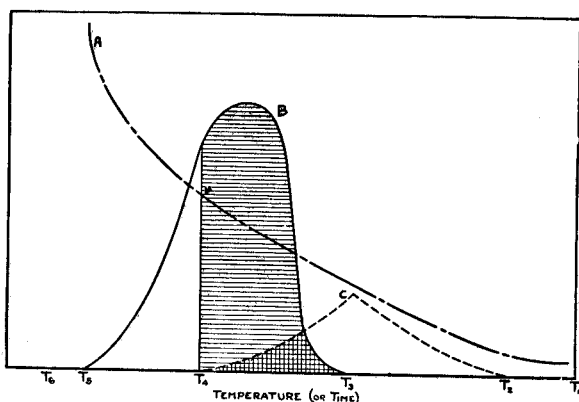
Fig. 1. Crystallization curves for spontaneous opal glass.

glass at a relatively high temperature, T_1, such as that obtaining when the glass is molten and in the pot or furnace, is transparent, because all of its constituents are in solution. It remains transparent until cooled to temperature, T_3, because, even though it has passed through the temperature range, T_2 to T_3, where crystalline growth is possible, none occurs because the crystalline nuclei necessary for the formation and growth of crystals, are wanting; that is, the glass is supercooled. From temperature T_3 to T_4 nuclei form, and the crystals grow so that the glass is rendered diffusing. Below temperature T_4 no further effective crystallization occurs because the glass on cooling becomes highly viscous and solidifies without further change of diffusing properties other than those which result from the variations of such properties as the refractive indices with changes of temperature. Since a relatively small section of a time-temperature curve for the cooling of glass approximates a straight line, the abscissa may be considered either as time or temperature for Figures 1 and 2, if proper proportionality factors are used. The actual curves for the several properties as a function of time really differ so slightly from those for temperature as hardly to justify the consideration of a second set of curves. On this basis the entire horizontally hatched area in Figure 1 is proportional to the number of crystals present per unit mass of opal glass. Similarly, the cross-hatched area yields definite information as to the maximum size of the crystals developed. A fairly satisfactory estimate of the size distribution of the crystals may be obtained readily by considering the vertically and horizontally hatched areas in relation to each other.

These considerations indicate that the diffusing properties depend largely on the rate of cooling of opal glass and that quite a range of sizes of crystallites is formed in opal glasses of this type. Unfortunately the temperature ranges, which determine the size and number of crystallites, overlap those in which the glasses are formed or shaped by hand as well as mechanical processes. This results in even greater variations in those factors which determine light diffusion in different parts of the same piece of glass. These relations are further complicated by the fact that there are frequently two, or possibly more, species of crystal-

lites present, each of which has characteristic relations like those de-
picted in Figure 1. Although much can be accomplished by efforts to
separate the crystallization temperature ranges from those in which the
glass is formed, or by properly shaping the hatched areas under the
curves, the practical limitations are evidently great.

Controlled Formation of Crystallites

A more satisfactory method is offered by the possible reduction of the
hatched areas to zero—that is, by the separation of the curves so that
these processes do not appreciably overlap, and the nuclei form only
below the temperatures at which the glass is shaped. On first consid-
eration this may not seem feasible, since the rate of nucleus formation
and the velocity of crystalline growth are both dependent on such
closely interrelated factors as:

1. The number of crystalline substituents (molecules, atoms, or
   ions) per space lattice element
2. The orientation of the crystalline substituents
3. The kinetic energy of the crystallizing substituents
4. The viscosity of the glass
5. The concentration of the crystallizing substituents
6. The magnitude of the energy changes involved (latent heats of
   crystallization or solution)
7. The thermal conductivity or rates of transfer of heat to or from
   the region of crystallization
8. The rate of diffusion to or from the region of crystallization
9. Interfacial concentrations (adsorption)
10. The influences of polar forces
11. Variations in the fugacities of crystallites with their radii of
    curvature, etc.

However, the relative influences of these factors and particularly the
roles of the last cited probably make it possible to obtain glasses yield-
ing a single species of crystallites whose characteristic curves may be
represented as in Figure 2.
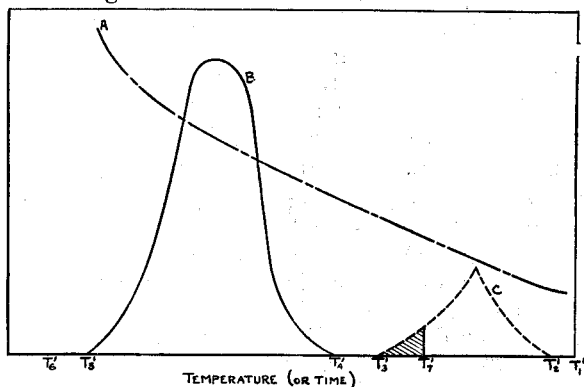
Fig. 2. Crystallization curves for controlled opal glass.

Opal glasses of this type may well be termed "controlled opals." On removing such a glass from the furnace, it cools from temperature T_1' to T_4' before nuclei start to form. It is then below the temperature range conducive to crystalline growth. The number of crystallites may be determined by fixing the time during which the glass is held within the range of curve B. Crystallites of definite and uniform dimensions may be obtained by reheating the glass to a temperature such as T_7'. Their dimensions are proportional to the areas included under curve C between the temperatures T_7' and T_3'. If the rate of heating of the glass is identical with the cooling rate previously considered, twice the integral under curve C between the limits T_7' and T_3' is proportional to the value of the radii of crystallites formed in the glass. The resultant crystals are of uniform and definite size in contrast to the wide ranges of sizes obtained in the spontaneous opal glasses previously described, since all of the nuclei are formed before growth begins. This affords a method for obtaining opal glasses of uniform and predetermined diffusing, transmitting, or reflecting properties.

Application of Controlled Crystallization

The application of the described conceptions has resulted in marked improvement and better control of the properties of illuminating glasses which are of generally uniform structure. This has been true of the
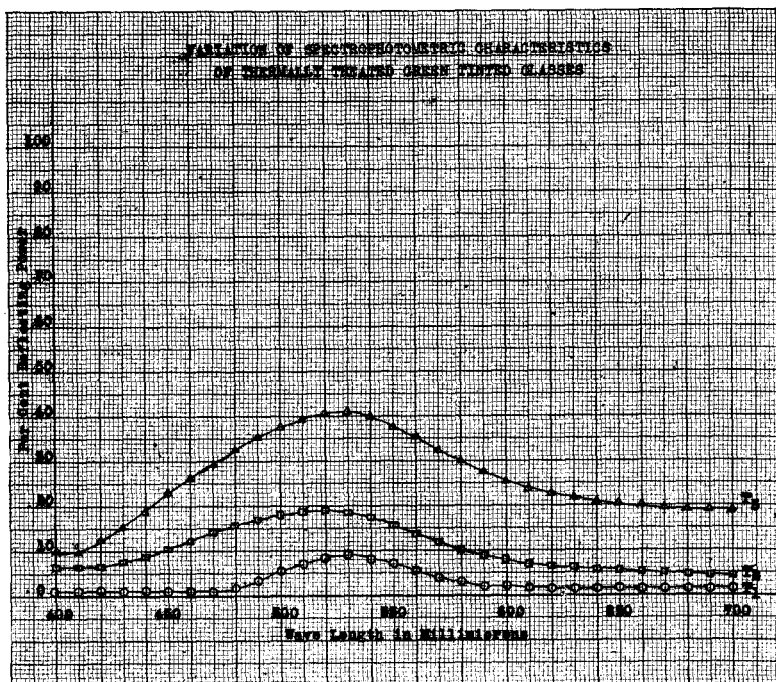
Fig. 3. Variation of spectrophotometric characteristics of thermally treated green tinted glasses.
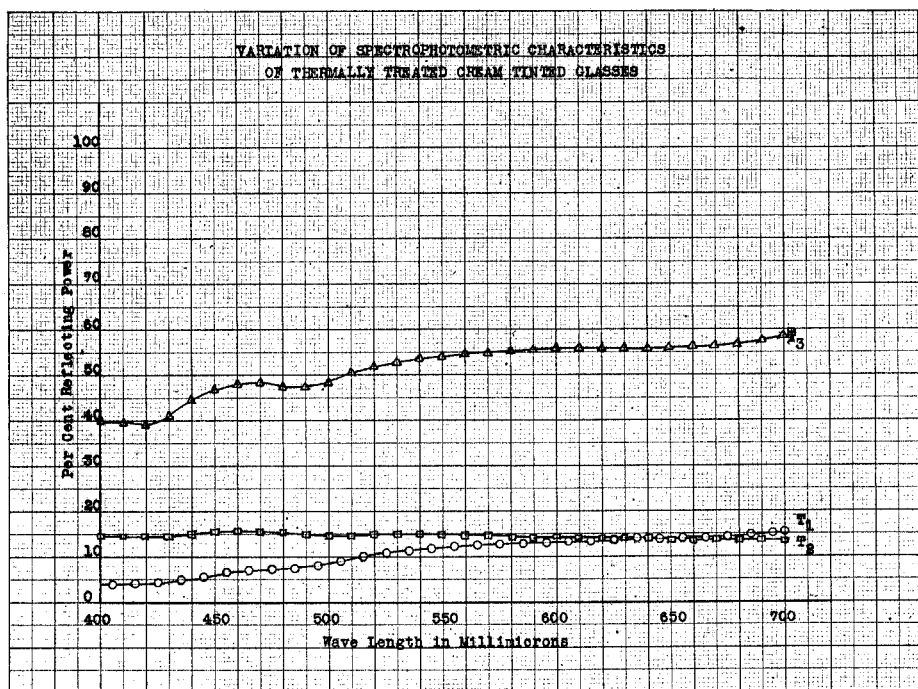
Fig. 4.   Variation of spectrophotometric characteristics of thermally treated cream tinted glasses.

spontaneous opals, although the more outstanding results have been attained with the controlled opals.   Semi-indirect lighting bowls have been produced which have illuminating efficiencies with extremely low brightnesses in spite of their use with high wattage lamps at small distances from the glass surfaces.   These glasses in ⅛-inch thicknesses yield coefficients of reflection greater than that of polished chromium plating.   The characteristics of these special glasses may be most satisfactorily illustrated on the basis of the photometric analyses of lighting units incorporating them.

In the glasses considered up to this point, the absorption coefficient μ has amounted to negligibly small values.   However, for colored glasses the values of μ are significant, and the dimensions of the crystallites then exert important influences on the brilliance, hue, and saturation of the glasses.   Figures 3 and 4 represent the changes of the spectral distribution characteristics of two glasses of this type.   These curves represent the reflectivity for the visible wave lengths. T_1 represents the data for a specimen of each glass which has been cooled by normal annealing, T_2 represents these relations for the same glasses after heating in an electric furnace at 1100°F for 15 minutes, whereas T_3 represents the data for the glasses when heated for the same period at 1200°F.   These data indicate the importance of definitely controlling the sizes of particles

(and other factors influencing the diffusion) in tinted or colored diffusing glasses, enamels, and glazes.

There is some evidence in the data for the Cream tinted glass of another important kind of color change which results from heat treatment. This type of change occurs in transparent, as well as in diffusing glasses and is characteristic of those glasses which contain as coloring agents, elements such as iron, copper, chromium, manganese, etc. The marked variations of color resulting from different thermal histories, apparently result from the presence of these elements in different states of oxidation. The equilibrium of the various oxidized forms seems to be displaced as a result of different heat treatments. There are also the possibilities that intermediate distortions of the electronic shells may take place with resulting variations in color intermediate to the extreme electronic shifts which are ordinarily attributed to a change in the state of oxidation. Similarly, color changes which have been induced in glasses by exposing them to radiation, may be reversed or neutralized by heat treatments.

The influence of heat treatment on color is even more striking for those glasses whose coloring agents are ordinarily believed to be in colloidal form. Of these, the Red glasses afford interesting examples. X-ray studies have given some indications as to the structure of these
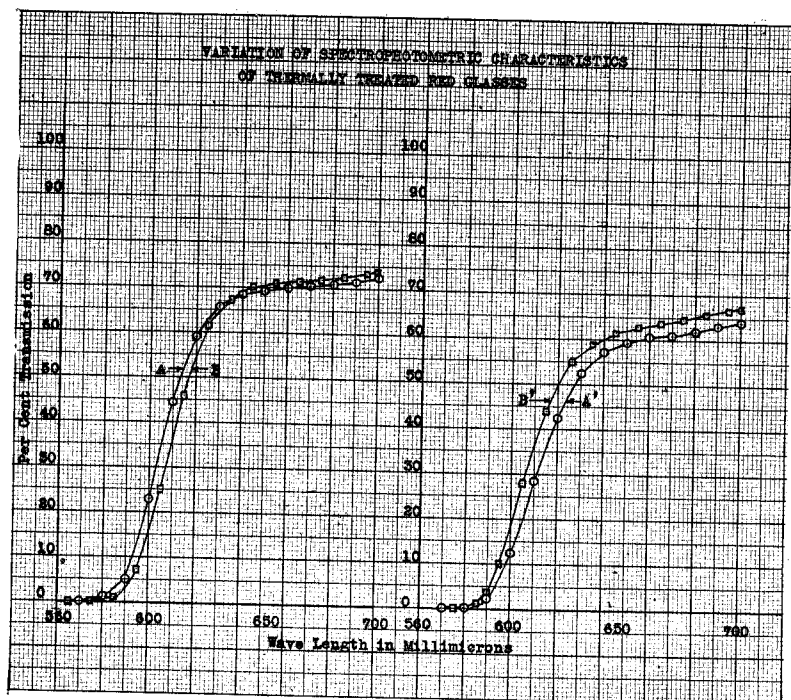
Fig. 5. Variation of spectrophotometric characteristics of thermally treated red tinted glasses.

glasses. C. Gottfried has thus shown that the coloring particles in Copper-Ruby glasses consist of crystalline, metallic copper. Rooksby has similarly shown the presence of elemental gold particles in Gold-Ruby glasses. Bigelow and Silverman, and Rooksby have independently identified the coloring particles in Selenium Ruby glass as solid solutions of cadmium sulphide and cadmium selenide. In such glasses, the coloring particles apparently constitute about 0.5 per cent of the glass by weight. Rooksby has concluded that increases in the sizes of the particles may take place "without visual color changes," at least within certain dimensional ranges. He has expressed uncertainty for these relations in the transitional size ranges.

However, it seems unwise to generalize concerning Selenium Ruby glasses. For example, it has been ordinarily concluded that the more intense the heat treatment, the deeper the Red color of the glass; in other words the higher the percentage of Cadmium Selenide in the solid solution. The spectral distribution data for two similar glasses subjected to the same heat treatment are illustrated in Figure 5. The curves marked "A" in each case show the relations between transmission and wave length for a glass heated for 15 minutes at 1200°, whereas the curves marked "B" show the corresponding relations for the same glasses heated for 15 minutes at 1250° F. The arbitrary integral comparison values for these glasses indicate their relative transmissions, which are as follows—

$$A \quad — \quad 140$$
$$B \quad — \quad 178$$
$$A' \quad — \quad 205$$
$$B' \quad — \quad 165$$

These data show that the transmission may actually be increased by raising the temperature (or the "intensity") of the heat treatment.

Many of the phenomena associated with Red and Yellow glasses may be explained on the basis of the same crystalline growth hypothesis of Tammann, which was previously applied to opal glasses. The spontaneous crystallization curves correspond to the behavior of those glasses which are usually described as "red in the pot." The uniformity of color and control of this type of glass is far from all that is to be desired for most purposes, but such glasses have the advantage of being more directly adaptable to the usual manufacturing processes. However, the controlled type of Reds are capable of yielding more precise and more readily reproducible spectral distribution characteristics. As a result of the probable presence of more crystalline species, the problem with selenium Red seems more complex than is the case with fluoride opals. Further evidence of the probable similarity of these phenomena lies in the fact that the controlled types of fluoride opals and selenium Ruby glasses may be converted into the spontaneous types by increasing the concentrations of the respective characteristic constituents in the controlled types of these glasses.

The preceding discussion indicates in a general way, the importance

of heat treatment in determining the properties of light modifying glasses. Several types of processes have been indicated in their broader technical aspects. Further studies in these fields should yield invaluable information to assist in clarifying the theoretical aspects of these problems and in serving as the basis for more refined technical developments.

DISCUSSION

DR. FRANK W. PRESTON, *Chairman*

HAROLD E. WHITE: (Pittsburgh Lava Crucible Company, Zelienople, Penna.): Is there anything in ceramics analogous to age hardening in metals?

MR. BLAU: It may be suspected that there are some analogies between age hardening of metals and the controlled formation of Crystallites in Opal glasses. However, the essential differences in structure of metals and glasses are such as to prevent the extension of more recent hypotheses of age hardening metals to cover glasses and most ceramic materials.

It is not improbable that the dependence of the properties of glasses on their thermal histories as described by Dr. Littleton, may be amenable to explanation on the basis of crystallite formation of the type described for Opal glasses. Such crystallites may exist in apparently transparent glasses without detection if the differences of the indices of refraction of crystallites and glass matrices are relatively small.

DR. NELSON W. TAYLOR: If we agree that age hardening in metals follows unmixing of a solid solution due to cooling, we may expect such effects in the systems CaO—ZrO_2, Ca_2SiO_4—Fe_2SiO_4 and nephelite—anorthite, which show a positive relation between solid solubility and temperature. The problem of solid solution unmixing has been studied in some detail by Dr. G. M. Schwartz at the University of Minnesota, particularly on the systems chalcopyrite-cubanite and bornite-chalcocite. Combinations of magnetite and ilmenite also show intergrowths on cooling of the homogeneous solid solution. Perhaps the best known case in the ceramic field is the so-called perthitic structure of sodium-potassium feldspars. Cases of this kind are undoubtedly numerous and study of solid solutions will bring them to light.

Effect of Temperature Treatment on Abrasives and Abrasive Products

BY ROSS C. PURDY

General Secretary, American Ceramic Society, Columbus, Ohio.

ABRASIVE wheels and blocks require an abrading element that is hard and of such a structure as will permit of surface or edge fracturing when abrading the object being ground or polished, the degree of fracturing required being dependent on the physical characteristics of the material being ground and the results desired. To grind and polish effectively and to obtain the vastly different results desired necessitates a variety of characteristics in abrading materials, a large number of combinations of abrasive grain sizes, a variety of bonds each with its own distinctive grain-holding characteristics, a large variety of degrees of "hardness" of the abrasive-bond unit, and several structural differences. These are the several variants which should be very definitely determined and controlled in order to produce an abrading tool which will accomplish most efficiently the grinding or polishing of a given object.

The physical characteristics of the material are not the only factors which determine what combination of the several variants shall be used in the make-up of the abrading tool. The size and shape of the object to be ground or polished and the results desired are factors in determining by what method the abrading can most economically be done. This involves precision and machine speed variants of abrading tool characteristics.

The object of an abrading operation is to most economically accomplish a desired material removal or a desired finish. The vast variation in materials, dimension, and shape of objects, and the finish required is the reason for the large variety of grinding tools and grinding machines, and the number of inventions in both grinding tools and grinding machines granted each month in each of the several industrial countries.

With this brief squint at the complexity of the abrasive problem, we will now more briefly look at the reasons for the demands for abrasive tools. The economic reasons for grinding will not be here viewed because there are not within the purview of this occasion.

When a cylinder is ground it is perfectly cylindrical, whereas, if trued by a single pointed tool in a lathe it will be "out of round." This true cylinder by grinding makes possible the working of the ponderous gates in the Panama Canal locks which with lathe turned hinge pins were not movable. Shredded wheat biscuits were producible only on ground cylinders whereas before their use, the wheat wrapped around the lathe turned rolls. Rotary parts of motors and valves of internal combustion engines are possible only because of being made perfectly

cylindrical by an abrading tool. Grinding, rather than turning axles and journals for railroad cars, has practically eliminated the ''hot box'' liability and has effected a saving in babbitt sufficient to pay all tool investment and labor cost of grinding. ''Flat wheels'' are less frequent on railroads since the wheel tires are being ground. Indeed, the role of the abrasive tool in the advances made in transportation and industry is a fascinating, dramatic story.

Not alone for rotary parts are abrasives found to be the most effective tool available. In cutting stones and metals and in polishing all sorts of objects, abrasives are being employed to a constantly increasing extent even for grinding flour, paint, and chocolate products.

The particle abraded from an object is a smaller sliver than that which is plowed off by any other tool. Since the physical characteristics of the material being abraded and the size of sliver desired determines the speed, power, and strength of the abrading particles required, so do they determine the combination of abrading tool variants which are most suitable. It is some of these abrading tool variants which are to be considered in this presentation.

Alumina Abrasives

Natural—Nature provides emery, corundum, and other mineral substances usable as abrasives where either severity or exactness of performance are not required. Of these natural abrasives, the only ones suitable for use in vitrified bonded wheels are emery and corundum. However, the variable composition and physical characteristics of emery and natural corundum make them unsuitable where exactness, constancy, and maximum efficiency in grinding performance are desired. Even for rough snagging, therefore, it has been found economical to make corundum abrasive grains by fusing emery, natural corundum, or other high alumina raw materials such as bauxite, purifying the melt and cooling in such a fashion as to produce a product which uniformly and constantly possesses definite desired properties.

Artificial Corundum Ingots—The ''impurities'' in the ore used for making artificial corundum have a profound effect on the physical properties of the abrasive produced. Iron added to wash out the silica as ferro silicon does more than remove the silica, it influences the crystallization. Any impurity such as titanium which does not have sufficient specific density and fluidity to separate out from the ''cast'' will remain as interfacial glass in the corundum, the variable distribution and composition of which causes a variation in character of the corundum. A study of equilibrium diagrams will show that all impurities in a $95+$ Al_2O_3 melt will be present only as a glass between the corundum crystals.

Impurities which will volatilize at the temperatures and under the conditions of electric furnace fusion of corundum will leave vesicular structures sometimes very generally and evenly distributed throughout the mass, and result in an abrasive grain of a peculiar and for several

purposes desirable sort such as in the white abrasive obtained by fusing alumina hydrate which contains a quantity of alkalies.

Heavy duty abrasive corundum grains are obtainable only when the electric furnace corundum ingot is a compact mass of alpha corundum crystals practically free from interfacial glass and cellular structure.

Light duty corundum abrasive grains are produced by the impurities in the raw materials used which form a rather thoroughly diffused glass interface, a cellular structure, and rarely is it practical or possible to obtain a satisfactory light duty corundum abrasive by batch additions, due to the difficulty of obtaining in the raw batch a uniform distribution of the materials which result in the interfacial glass or in the cellular structure.

A "softer" abrasive grain midway in properties between the heavy and light duty is producible in electric furnace corundum by "boiling" the fused mass with alkali salts added to the raw batch, or by mechanical stirring.

"Sintered corundum" made by heating Al_2O_3 or corundum powder sufficiently to cause the mass to sinter and to transform to alpha corundum but not become molten, will not produce an abrasive which will have a general application because it lacks mass strength and uniformity. Sintering will produce alpha corundum but will not produce the desired compact, hard, and strong alpha corundum required for abrasives. The mass must be heated to a liquid fusion in order to secure a requisite growth of individual crystals, a required compactness of crystals, a separating out of the ferro silicon, a segregation of the interfacial glass impurities, and a desired mass structure of the ingot. This is the reason why the brick furnaces even with 3-phase electrodes do not give as uniform a product as do the water-cooled steel-shell furnaces with 2-phase electrodes, for in the latter there is obtained a more uniform liquidity of the fusion and hence a product more uniform in purity and in physical character resulting from a more uniform thermal treatment throughout the mass of each individual ingot, and from ingot to ingot.

Reduction of Ingot to Grain Sizes—A 5 ton ingot is allowed to cool in an open shed, sledged to large chunks, jaw crushed, and rolled, producing particles ranging from 8 mesh to 200 and finer. The 24-mesh and coarser grains are split out from the finer grains, and further separated and cleaned by powerful magnets of all grains containing ferro silicon. The grains smaller than 24-mesh, because it is impractical to sufficiently extract from them the grains contaminated with ferro silicon, are roasted for the purpose of oxidizing the ferro silicon and the reduction products such as carbide. All grains, whether roasted or not are mulled in water to fracture off the adhering ferro silicon and oxidized products thereof, to reduce the grains to more "cubical" shape, and to break up the "flats" and "slivers" and to oxidize the carbides. This mulling increases the weight per unit volume of the grain.

Before alumina abrasive grains can be most successfully mixed with water, and particularly with glue, they must be treated either by fire

or by an alkali, preferably both, to increase their "capillarity" as measured by the height to which water will rise in a glass tube filled with the abrasive grain. To what this lack of possession of capillarity of the grain is due is not definitely known although oil has been distilled from freshly milled, untreated grains and the surface of the grain is known to carry a static charge of electricity.

Silicon Carbide Abrasives

Very tempting is it to write the history of silicon carbide. It is not found in nature. It was discovered by Acheson when attempting to make diamonds. Even its industrial production is intriguing. The heat history of silicon carbide and the methods employed in abrasive grain production have been given by several writers. Sufficient is it to say that silicon carbide is not a fused magma product. It is formed from vapors of carbon monoxide and silicon under strongly reducing conditions, so reducing in fact that most generally the silicon carbide is strongly impregnated with solid carbon and has graphite as interfacial material.

Silicon carbide will completely oxidize at 800°C in oxygen leaving only SiO_2. Any flux which combines readily with SiO_2 will, in oxidizing atmospheres, cause disintegration and oxidization of silicon carbides. It is readily attacked by fluorine. These are the reasons why silicon carbide presents more difficulty in bonding with fluxed clay bonds than do the alumina abrasives.

Silicon carbide ore is crushed, mulled, and screened to grain sizes the same as are the alumina abrasives. Some producers wash the grains in sulphuric acid before mulling and screening to remove the iron and to make easier the washing off of the adhering graphite. Silicon carbide grains are not roasted nor alkali treated.

Bonding Abrasive Grains

Both kinds of artificial abrasives are bonded with (1) fluxed clay, (2) silicate of soda, (3) shellac, (4) bakelite, and (5) rubber bonds. Except for the fluxed clay bonds, the bonding of the alumina and the silicon carbide are the same because the temperatures at which the other bonds mature do not exceed 450°F, at which low temperatures, silicon carbide is perfectly stable.

The purpose of the bond is to hold the grain while it is cutting the material being ground or polished. If the grinding work to be accomplished, and if the contours of the abrading wheel or stone need not be considered, the bond may be the more friable silicate of soda or shellac bonds. If strength and a fixed contour of the grinding medium are required, the bond must have a strength which is obtainable only with a fluxed clay, bakelite, or rubber bond.

There are several considerations, outside of the scope of our present interests, which dictate the type of bond which will render the most efficient service in a given case. We shall confine our considerations to

the fluxed clay bonds because these involve more accurate heat treatment problems.

Fluxed Clay Bonds

Corundum Bonds—Artificial corundum (Al_2O_3) in coarse grains is exceedingly resistant to chemical action of any sort even in fused magmas. Therefore, the problem of bonding corundum is the furnishing of strong, shock-resistant pockets or envelopes by which the grains of corundum are solidly held while they are abrading the material being ground.

The only temperature limitations in bonding corundum with fluxed clay bonds are (1) at 1390°C (cone 13) there is a weakening of the corundum grain and (2) cone 4 (1210°C) seems to be lowest heat treatment by which a sufficiently strong, glassy bond can economically be produced.

In the glassy bonds used for corundum abrasive grains there is, at cone 11 and higher, a slight development of mullite crystals apparently as a result of a fluxing action of the bond on the corundum crystal. This development of mullite in the bond can not be taken as being the cause of the weakening of the corundum.

One theory for the weakening of the corundum grains at cone 13 is that the glassy bond dissolves or leaches out the glassy interface material from the corundum grain. This weakening of the grain does not occur with bonds that mature at heat treatments ranging from cone 4 to cone 12, irrespective of the composition and physical characteristics of the bond. Furthermore, this weakening of the corundum abrasive grain at cone 13 occurs as certainly and to the same extent with bonds with and without a boric acid frit bond addition, and irrespective of the viscosity of the bond.

In connection with this question of mineral reaction between the corundum grain and the bond it is interesting to note that the only bonds which will solidly hold corundum grains are glasses high in Al_2O_3 such as the following:

	$(K.Na)_2O$	CaO	MgO	Al_2O_3	SiO_2
1.	0.29	0.43	0.28	1.9	6.5 (for soft wheels)
2.	0.55	0.28	0.17	1.2	7.5 (for hard wheels)

These glass bonds must glaze over the corundum grain without crazing or spalling. As glazes on clay products they would be considered very viscous and ''immatured'' even at cone 13 down. Certainly they do not attain that perfection of glassiness and completeness of mineral reaction sought and obtained in porcelain glazes and in glassware. In magmas so obviously far from completion in their possible mineral reaction and containing so high a content of Al_2O_3 there would seem to be little if any inducement for the glass bond to dissolve Al_2O_3 from the relatively coarse corundum grain; yet it is only with glassy bonds that

efficient abrading units can be made with corundum grains. Porcelain bonds not only make corundum abrasive wheels too dense for efficient cutting but they also do not hold the grains as strongly as do the immature glassy bonds.

Silicon Carbide Bonds—The only upper limit to the heat treatment usable in bonding silicon carbide abrasive grains is the maturing tem perature of the porcelain bond. If there could be found a porcelain producing mineral mixture which would not react with the SiC there would be no lower limit to heat treatment except that necessary to mature a bond to sufficient strength to make a serviceable silicon carbide wheel.

Several of the fluxes usable with corundum will dissociate SiC causing a liberation of CO which "boils" the silicon carbide wheels. Hence it is the practice to use a bond composed of ball clay, feldspar, flint, occasionally with talc, pyrophyllite, and other silicate mineral flux additions.

Black Coring—Black coring, or the production of a black center, in silicon carbide ware, is caused by entrapped carbon and results in a weakening of the bond. This black coring is analogous to the black coring in clay ware in which the carbon is not fully burned out before being sealed in by the sintering clay. The difference in the two cases is that in clay ware the carbon is originally in the clay as carbon and can be burned out at ignition temperature, whereas, in silicon carbide ware the carbon is liberated from the SiC beginning at 800°C. The oxidation period during which silicon carbide abrasive products when being kiln fired must be given a slower rate of temperature rise as between 800°C and 1000°C, or from cherry red through light yellow heat colors almost to white heat. This slow heating through this oxidizing period allows the carbon to oxidize and be vaporized as CO before the bond becomes too thoroughly vitrified. This slowing down in the raising of the heat of the kiln between 800°C and 1000°C will prevent black coring.

Conclusion

Since this conference is interested only in the heat-treatment problems of abrasives and abrasive products, the many coincident problems in abrasive production are not here considered. Indeed, the time and space limits of this presentation are not sufficient to adequately present the heat treatment problems.

The production of abrasive products to meet the exacting specifications of grain size, hardness, structure, and strength involves various bond compositions and contents, many abrasive grain size proportions, several methods of forming, and a variety of heat treatments, all of which are ceramic problems which require control much beyond the usual.

DISCUSSION

Dr. Frank W. Preston, *Chairman*

Dr. R. B. Sosman: Do beta and gamma alumina enter in the work on abrasives?

Mr. Purdy: We avoid them.

Dr. Preston: Mr. H. E. White has had a good deal of experience in the abrasives field. Perhaps he would give us some comments.

Mr. White: Mr. Purdy has implied that the object of an abrasive operation is to economically remove the undesirable material and to obtain the desired finish. The metals, which furnish the largest field for the use of abrasive products, are roughly divided into ferrous and non-ferrous groups. Similarly, abrasives are divided into two groups, aluminous abrasives and silicon carbide abrasives. These two groups apply respectively to the two metallic groups, however, there is considerable overlapping in both directions. In order to extend the use of each group over the territory of the opposite group, considerable variation in physical properties of the crude abrasives and in the subsequent treatment of the finished products has been made.

With aluminous abrasives the principal idea seems to be to control the size of the Corundum crystals and the amount and distribution of the intercrystalline glass, as well as to control to some extent the nature of the crystal itself.

The size of the Corundum crystal can be controlled by the size of the ingot being cast and by the rate of cooling to some extent. With the same size ingot, however, it seems that an increase in alumina content decreases the average size of the crystals themselves. This is undoubtedly due to greater agitation of the bath due to the refining operation.

Changing the nature of intercrystalline glass seems also to affect the size of the Corundum crystals produced.

The nature of the Corundum crystal may be varied by addition of impurities which will either volatilize at the temperature of the fusion of alumina or will be left as a constituent of the intercrystalline glass after having been active during the melting stage. Thus we may produce at will Alpha or Beta Corundum with or without vesicular voids piercing the crystals themselves.

Reduction of Ingots to Grain Sizes

Considerable research work has been done on the reduction of crystalline alumina to grain size. One process so modifies the intercrystalline glass that it is water soluble and may be leached out with the help of weak acid and permits the alumina crystals to be separated as such. Unfortunately the size of these crystals is so small as to make the process at the present time limited. The usual method is to break up the large ingots in the orthodox way and crush it down to one half inch and finer

in jaw crushers. From this point on, ideas are very much divided. Some companies disintegrate this material by means of special crushers which break the grain up into isometric particles having coherent structure and similar strength. Others use roll crushers and some sort of pan mill or muller to round out the grains and remove the flats and slivers.

The ultimate aim is to obtain a particle shape as near to a sphere as possible and have a maximum number of cutting edges on the surface of this sphere. The idea of the spherical shape is to provide a minimum volume with a maximum weight and resulting maximum strength. In the process of manufacturing abrasive wheels, it is necessary to separate the abrasive grains so that they are divided into lots, each lot consisting of grains of as nearly the same size and shape as possible.

Theoretically, if the grain is sized correctly, and is spherical the same volume of the 8 mesh materials will weigh exactly the same as the same volume of the 24 mesh material. This of course is a mathematical truth.

Mr. Purdy has described the removal of iron particles and ferrosilicon by means of the electro magnet. A variation from this method is that of treating the grain with chlorine gas and the distilling off of the metallic impurities of iron, silicon and titanium as chlorides of these metals. The heat generated by this process is sufficient to carry off some of the oxides of these impurities and some alumina as well, thereby appreciably purifying the abrasive. 94 per cent alumina material may be easily increased to 98.5 per cent.

Another method of similarly purifying the abrasive is to treat it with mixed acids of which a small percentage is hydrofluoric acid.

Mr. Purdy has stated that a weakening of the Corundum abrasive grain occurs at Cone 13. There is undoubtedly, as he states, an interaction of the intercrystalline glass. Prolonged roasting at temperatures above Cone 13 will cause some of the intercrystalline glass to exude to the surface of the particles and the red color of the usual 94-95 per cent Al_2O_3 aluminous abrasive will be changed to a dark blue.

By alternate roasting and etching with the above mentioned mixed acids an appreciable portion of the intercrystalline glass may be brought to the surface of the grain and removed, and the grain thereby purified to above 98 per cent Al_2O_3. By this process, a noticeable proportion of alumina is of course removed as the intercrystalline glass is principally made up of aluminates of the existing impurities.

Some alumina refractories using a large quantity of crystalline alumina and a small proportion of bond actually undergo an appreciable expansion when fired to Cone 20 or above. Investigation indicates that there is an appreciable absorption of the clay bond by the intercrystalline glass.

Mr. Purdy has stated that before aluminous abrasive grain can be most successfully mixed with water and particularly with glue it must

be treated either by fire or by an alkali.   The firing or roasting of this material may be done at a reasonably low temperature, approximately 1800° F.   The abrasive grain undergoes a surface change which by some has been attributed to a re-oxidation or increased oxidation of the surface minerals.   It is sufficient to say that irrespective of the burning off of any oil picked up in the process the surface of the grain is given a dull finish so that it is easily wet by water.

Silicon Carbide Abrasives

Silicon carbide abrasive grain has metallic silicon as well as carbon as intercrystalline material.   By taking a normal silicon carbide grain and mixing it with caustic soda and fusing the same, and later dissolving out the grain it will be found that the silicon carbide grain is perforated with holes and somewhat disintegrated due to the silicon being dissolved. Naturally there is some loss of the silicon carbide itself in this operation, however, a vastly different product results and a rather impure silicon carbide can be appreciably purified by this method.

Silicon carbide also is used to a considerable extent in the refractory industry.   Its formation is a very interesting process.   In graphite crucibles which consist approximately of 50 per cent graphite and the balance bond clay, silica sand and, or silicon carbide, it is possible under certain conditions to generate silicon carbide whether or not silicon carbide was present originally.   If the temperature of the crucible is raised sufficiently high the carbon will react with the silica of the bond or the added silica and form amorphous silicon carbide.   It has been known to have generated as high as 30 per cent SiC in a normal graphite crucible in addition to any SiC originally present.   This generation in the crucible wall is accentuated in the presence of iron or nickel slags. The temperature of the crucible during this formation need not be especially high and may be in the neighborhood of 2800 to 3200° F.   This temperature is of course far below the actual formation of crystalline silicon carbide.

Carbon rods may become impregnated with silicon and form a solid rod of silicon carbide.   Silicon carbide may be re-crystallized in brick form without bond.   The brick is formed with a temporary bond and inserted in the furnace subject to the gases of the furnace.   When the brick is removed it is in the same form as it was put in the furnace but is re-crystallized and the temporary bond burned out, being replaced by the re-crystallized bond of the silicon carbide.   Re-crystallized products such as these, however, cannot release the grain once it has been dulled. Abrasive materials must be released of their bond as soon as they are dulled and then the abrasive must present a new cutting edge to work. Otherwise the abrasive process will be impractical.

MR. PHELPS: Why is beta alumina said to be less stable than alpha?

MR. PURDY: Beta can go to alpha, but alpha cannot go to beta, or the action is very slow.

MR. WHITE: Beta forms in presence of lime or soda, according to Klein.

DR. SOSMAN: Merwin finds it in magnesia melts. There is evidence that beta alumina is not one hundred per cent Al_2O_3.

INDEX