DEVELOPMENT OF NUCLEI AND GROWTH OF $Zn_2 Ti_3 O_8$ CRYSTAL IN A ZINC FORCELAIN GLAZE (a composite material)

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ABSTRACT

The crystallization behaviour of a zinc raw glaze was investigated. In addition to the expected willemite crystals, a new crystal, $Zn_2TiO_3O_8$ was identified. This was a gold coloured angular crystal on a blue background of cobalt. It develops on cooling at about 1100°C. This is the first time this crystal is reported in a glaze.

In an attempt to make experimental results clearer kinetic reaction, nucleation and crystallization theories and glazing procedures are reviewed in this paper.

KEYWORDS

Zinc crystalline, glaze, nucleation

INTRODUCTION

The purpose of this research is to explore the possibility of developing a zinc crystalline glaze from non-fritted ceramic materials.

Numerous scientific investigations have been made into crystalline glazes the results of which have been recorded in the literature, [1-7]. However, most of these investigations were made on fritted crystalline glazes of commercial possibilities.

The research also has as its aim developing a useful raw crystalline glaze of commercial possibilities for use by the small traditional ceramic operations as well as the large industrial manufacturers; a glaze that matures with the body in a single fire, does not flow off the ware, does not craze, and produces crystals of a pleasing habit that are consistently producible within limits both as to size and number.

REVIEW OF NUCLEATION AND CRYSTALLIZATION THEORY

From time immemorial potters have been producing visible crystals in the glassy matrix of glazes. The first appearances of these crystals were, doubtless, accidental hence there was no control over the crystal formation nor growth of these crystals.

This art of crystal formation later in the years past became a scientific investigation. Many investigations had been made over the years before 1940, and there were successes to enhance aesthetic qualities not only of studio pottery but also industrially produced whitewares.

Since the writer is dealing with complex mixtures of oxides, he has chosen to relate reaction in the mixtures to chemical reaction theories to help make the behaviour of the constituents of the glaze or experimental results clearer.

The study of base silicate melts belongs to the field of chemical kinetics which helps in understanding reaction rate phenomena. Chemical kinetics have been interpreted in terms of collision theory [8]. This theory makes basic assumption that in any chemical reaction, ions, molecules or atoms must collide. The collision theory, therefore, accounts for four basic factors which influence reaction rates [8] :

1. Concentration of reactions, because the number of collision increases as concentration increases.
2. Temperature, which when increased makes molecules move faster, collide more violently to promote reaction.
3. The nature of reactants; because energy of activation differs from one reaction to another.
4. Catalysts, the presence of which rate of reaction depends.

All the above factors in one way or the other assist in the choice of materials, working out the molecular proportions of these materials and temperature treatment to be given the overall compositions to achieve a desired result.

One other theory which must not be overlooked in the experimentation is the absolute-reaction-rate theory for which the collision theory of chemical kinetics is actually the basis. This calculates the potential energy change in a system as molecules come together to form activated complex. The rate theory explains the reaction path of each step such as individual atom jump in diffusion or new chemical bond being formed involving activated complex or transition state of maximum energy along the reaction path. Figure 1A explains this reaction theory.

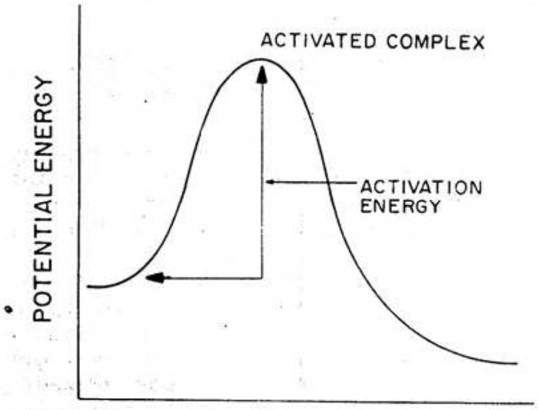

Figure 1A Reaction Rate

In many processes, however, the specific reaction rate is related to temperature by the relation,

$K = Ae^{-E/RT}$

where A = a constant characteristic of reaction,

e = natural logarithm base, 2.718,

E = an energy called experimental activation energy of reaction, and

R = the gas constant equal to 1.987 cal/mole $^{-1}$ deg $^{-1}$

At this point, the author wishes to stress that this experiment is not set to prove chemical reaction rate theory nor the absolute-reaction-rate theory.

With the scanning of chemical theories on reaction rates, we consider the chemical thermodynamic property Entrophy, S, which measures randomness in a system. According to the second law of thermodynamics, for spontaneous change in an isolated system, the entropy must increase, that isΔS must be greater than zero :

$$\Delta S_{TOTAL} = \Delta S_{system} + \Delta S_{surrounding} > 0 \quad ....1$$

The $\Delta S_{surrounding}$ corresponds to the amount of heat transferred to the surroundings divided by the temperature at which the transfer occurs. Heat added to the surrounding increases thermal motion and hence increases random disorder : this is then expressed,

$$\Delta S_{surrounding} = \frac{\Delta H_{surrounding}}{T} = \frac{-\Delta H_{system}}{T},$$

where $\Delta H_{surrounding}$ is the increase in the heat content of the surroundings due to heat transfer from the system to the surrounding. In the process the heat content of the system diminishes by the same amount; substituting,

$$\Delta S_{TOTAL} = \Delta S_{system} - \frac{\Delta H_{system}}{T} > 0 \quad ....2$$

On most occasions only what happens to the system is considered and not its surroundings. For the system alone, the second law states that the quantity which must increase in a spontaneous change is

This is related to the free energy change:

G = H - TS or free energy is,

$\Delta G = \Delta H - T\Delta S$ at constant temperature and pressure.

Dividing through by T gives,

$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$ or by changing sign and rearranging,

$$-\frac{\Delta G}{T} = \Delta S - \frac{\Delta H}{T} \quad ....3$$

For spontaneous change in a system in contact with its surrounding $-\frac{\Delta G}{T}$ must be > 0. This is shown in equation [2].

Before considering or discussing nucleation, it should be borne in mind that free energy of a substance as well as its heat content depends on the state of the substance. It also depends on the temperature and the pressure in the case of solution or concentration. Consequently, the change of the free energy during a chemical reaction depends on the state, conditions and concentrations of the reactants and products.

NUCLEATION

The earliest and most important studies of nucleation were done more than 80 years ago. In the solubility of materials Ostwald [9] and others showed that spontaneous crystallization takes place in only supersaturated solutions. They also developed the idea of a metastable zone within which no crystal nuclei could form spontaneously. This metastable zone has been confirmed by later experimental and theoretical investigators and has been shown to be true.

It is worthwhile defining crystallization before embarking on classical theories propounded from studies in this field:

Crystallization is the process by which the regular lattice of the crystal is generated from the less well-ordered liquid structure [10].

Theories on melts and crystallization are generalities based on classical studies [11]. A glaze like a glass is a complex mixture described as super-cooled solution [12]. Being a glass in its physical and chemical nature a glaze, therefore, necessarily takes advantage of crystallization theories.

Tamman [13] made classical studies of crystallization on supercooled liquids in 1925. His experimental studies of crystallization of under-cooled organic liquids and inorganic glasses lay classic bases of much of our knowledge on nucleation and crystallization.

During melting of bodies, the oscillating movements of the lattice building block around their lattice points or rest positions attain a certain magnitude at a certain temperature, which is referred to as temperature of fusion. A high amplitude of atoms results in the building block no longer returning to their former positions. The crystal lattice breaks down and it loses regularity. The silicate mixture melts and assumes a fluid state. As no further energy is being supplied the melting point of the silicate melt remains in equilibrium. If at melting-point the system is continuously supplied with further heat energy, the heat energy removes the lattice building blocks from the lattice points and thus raising the internal energy of the system by the amount of latent heat of fusion. No rise in temperature occurs as long as crystalline matter is available. On supply of energy, however, a further increase in temperature occurs when there is liquid phase remaining.

On cooling of the strongly heated fusion of the silicate mixture, thermal motion of atoms or molecules diminishes. Thermal contraction and an increase in viscosity ensue because of the crowding together of these atoms of building units and the strengthening of the bond between them. The liquid melt changes to crystalline solidification in which case the latent heat of fusion put into the system is given up in the form of heat of crystallization. Arrest point also occurs in this case on the cooling curve until the whole melt is completely solidified.

Tamman showed that below the equilibrium melting temperature there exists a temperature interval referred to as the "metastable" zone [14] in which nuclei do not form at a detectable rate. In this zone crystals can grow if nuclei are provided. Melts which increase in viscosity on cooling show maxima in crystal growth rates. This is because lower temperature promote high viscosity which hinders the atomic rearrangements and diffusion processes which are necessary for nucleation and crystal growth.

Tammann's theory based on the thermal agitation of a'toms has been the basis of research on crystalline glazes. He has shown that the formation of visible crystals depends upon three conditions :

1. The number of nuclei formed (KZ)
2. The rate of growth of the crystals (KG)
3. The viscosity of the melt.

These conditions are illustrated in Figure 1B. This diagram could as well be drawn as in Figure 2A. In Figure 2A $(T_1 - T_2)$ shows the "metastable" zone of supercooling. The temperature zone below T_3, of low nucleation rate can be regarded as another "metastable" zone.

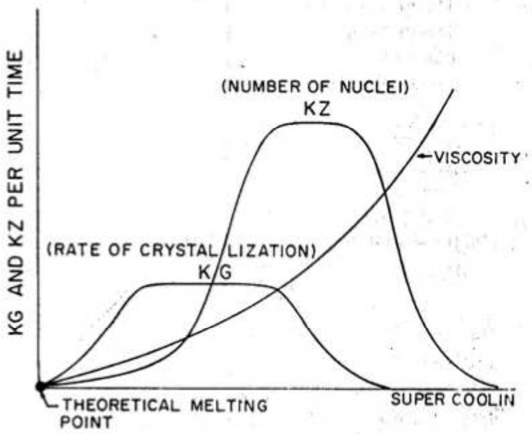

Figure 1B Dependence of Nucleation (KZ) and Growth of Nuclei (KG) on the undercooling of Glass Melt after Tam man

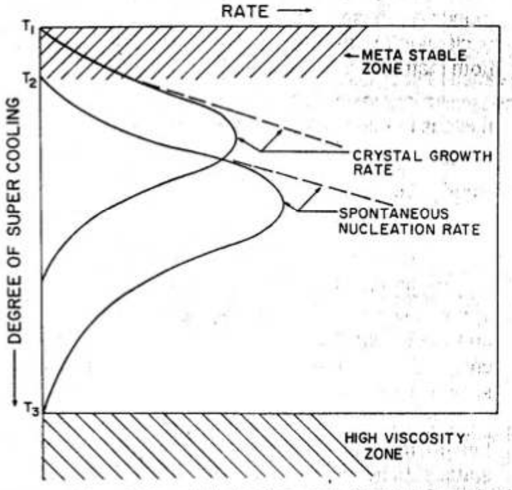

Figure 2A Rate of Nucleation and Crystal Growth of different Temperatures

In order to form a new phase (the nuclei) within a mother phase, an increase in free energy of the system must occur; this constitutes a barrier to nucleation. Groundwork for theoretical studies on the basis of thermodynamic equilibrium relating to studies of nucleation was laid by J. W. Gibbs in 1928 [9]. This notion of thermodynamic equilibrium can be used to derive relations for critical size of nuclei. Gibb's derivation of the work of formation, W, of a critical nucleus of phase B in a mother phase A shall be shown later. Other parameters to be considered in discussing nuclei formation are :

1. The growth of a new phase B at the expense of initial phase A can occur only when they are not in equilibrium. During the change, therefore, A is in metastable equilibrium with respect to B.

2. The nuclei formed of phase B are very small particles of B. They differ from larger particles because of their large surface area, and therefore surface energy and surface tension.

The nucleation rate I of a crystal is given as,

$$I = K \exp \frac{W}{kT} \qquad \text{----4}$$

where k is Boltzmann's constant.

The effect of composition and temperature, T on K is small and the work of critical nucleus formation W* for a spherical isotropic nucleus is,

$$W^* = \frac{16\pi\gamma^3}{3(\Delta P)^2} \qquad \text{....5}$$

γ is the interfacial tension and P is the pressure difference between the interior of the nucleus and the surrounding phase, and is called the driving force of nucleation of free energy change per unit valume going from matrix to critical nucleus.

An approximate equation for ΔP for a crystalline nucleus forming in a liquid or glass is,

$$\Delta P = \frac{L}{vT_m}(T_m - T) \qquad \text{----6}$$

where Tm is the melting temperature,

L is the heat of fusion, and

v is the molar volume of the liquid.

Therefore, it can be discerned that two parameters in determining nucleation rate are the interfacial tension γ and the driving force ΔP. Lowering the temperature increases P and consequently I [15], the nucleation rate, shown in equation [4].

When a crystal nucleates, there are two sources of free energy change. First, the formation of a boundary or surface between the embryo and the mother phase results in a gain of free energy due to the interface energy.

Secondly, since the arrangement of the atom within the embryo will be less disordered than that in the surrounding phase there will be a reduction in free energy of the system. Thus the two opposing factors which govern actual free energy change can be written in the following way to give ΔG, the free energy change for a spherical inclusion of radius r :

$$\Delta G = -\frac{4}{3}\pi r^3 \; \Delta G_v + \Delta r^2 G_s$$

where ΔG is the free energy change per unit volume resulting from transformation of one phase to the other, and ΔG_s is the energy per unit area of surface between two phases.

The above equation shows that when r is small the interfacial energy term predominates, but when the radius of the embryo increases the interfacial energy becomes a small fraction of the total change. Once some critical radius is reached the volume free energy term predominates and further growth will lead to lowering of free energy and therefore to a more stable system. At a given temperature the overall free energy change is related to the radius of the nucleus in the manner shown in Figure 2B. This figure explains the change in overall free energy as a nucleus grows. Regions smaller than the critical radius (embryos) require an increase in free energy to form and will continually form and dissolve with the total number in the system remaining constant. Some embryos will attain the critical radius and will continue to grow with a decrease of energy and hence will constitute stable nuclei. At the critical radius, the free energy attains its maximum value.

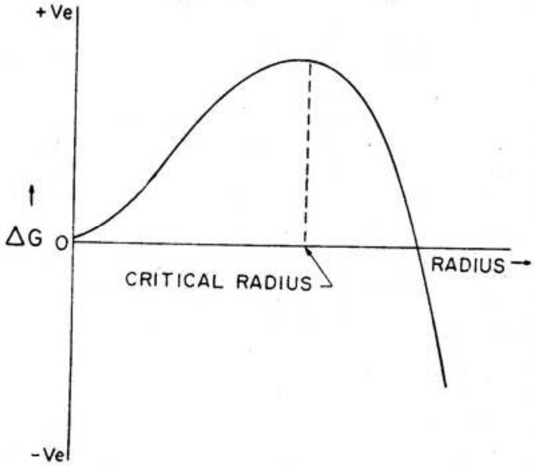

Figure 2B Charge in Overall Free Energy as a Nucleus Grows

An expression has been derived for homogenous nucleation by Becker and Doering [1] and Frenkel [2] and others have applied statistical mechanics to the expression,

$$I = A \exp(-\Delta G^*/kT)$$

where A is a constant and ΔG^* is a maximum free energy of activation for formation of a stable nucleus.

The above expression neglects the effect of diffusion rate. In viscous liquid however, diffusion of molecules across the phase boundary may constitute a major barrier to nucleation. A general equation for the the rate of homogenous nucleation in condensed system proposed by Becker 1 gives a better approach:

$$I = A \exp\left[-\frac{(\Delta G^{*} + Q)}{kT}\right]$$

where Q is the activation energy for diffusion of molecules across the phase boundary.

This theory provides a quantitative explanation for experimental observation.

In heterogeneous nucleation, the important feature is that the interfacial tension between the heterogeneity and the nucleated phase must be low. The influence of the catalysing surface is therefore the angle of contact, O, at the substrate-melt-precipitate junction. The activation energy for this system is expressed,

$$I_C = A^1 \exp[-\Delta G^{*} f(\theta)/kT]$$

and when activation energy of diffusion, Q, is included we have,

$$I_C = A^1 \exp[-(\Delta G^{*} f(\theta) + Q/kT]$$

With the general theories discussed, one must consider the following when studying crystalline glaze:

solubility of oxides used, degree of saturation and viscosity.

It has already been mentioned that for crystallization to begin, a nuclei must be formed. For this reason special importance must be attached to the transitional region between a liquid melt and a solid. In a glaze melt no spontaneous nucleation occurs if the saturation curves are slowly exceeded. This phenomena is shown schematically in Figure 3. On cooling of a melt which is at temperature x, spontaneous formation of nuclei and crystals only takes place when a second boundary, the super-saturation curve has been transgressed. This intermediate region called Ostwald-Meirs region cannot be exactly determined. A crystal introduced into this region will continue growth, but there is a certain threshold for nucleation.

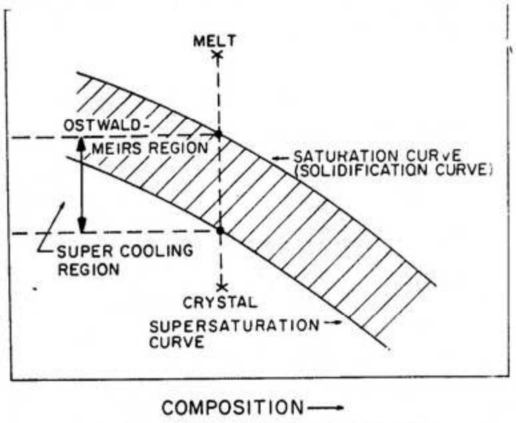

Figure 3 Schematic Representation of the Transformation of Highly Viscous melt into Crystalline state.
(This drawing is based on the Theory of Kleber and Roy (1D)).

On the whole, however, theories proposed to explain growth of crystals from a melt are of varying complexity. Their validity is still a matter of considerable controversy.

LITERATURE REVIEW

As has been discussed in the previous sections, an added heat energy, the latent heat of fusion is necessary to effect melting; and equilibrium situation is determined by this free energy difference, $\Delta G = \Delta H - T\Delta S$. As can be discerned it is the greater randomness of the liquid than its greater enthropy which makes T ΔS term large enough to overcome ΔH so that the crystal melts when T ΔS = ΔH. It must also be remembered that heat exhanges during fusion are endothermic during evaporation, dissociation, inversion and melting.

EFFECT OF TEMPERATURE ON CRYSTALLIZATION

Crystallization is strongly influenced by temperature; this is discussed in Section II. As shown in Figure 2, when the temperature is lowered below the equilibrium temperature the nucleation rate and crystal growth increase and then decrease; there is decrease because of decreasing mobility of atoms resulting from increasing viscosity.

EFFECT OF CONCENTRATION UPON GLAZE

Since further energy is proportional to the surface area, finely ground particles fuse more easily than the coarse ones. This affects the viscosity of the glaze. We therefore see that fritted mixes fuse lower because of their homogeneity and because of the presence of previously fused materials.

The composition of the body has a remarkable influence on the appearance of the crystals due to the dissolution of the body constituents into the fluid glaze. Since body solution is an interfacial process the amount of body dissolved is almost constant for a given composition on a set firing schedule.

EFFECT OF COMPOSITION ON GLAZE

Many ceramicists have investigated composition variables in glaze have reported contradictory results. Impurity in the raw material can affect composition; Norton (1) stated that the composition of the body exerted strong influence on crystalline glaze. A glaze being a multicomponent variable, a substitution of one variable for the other will affect the nature and general composition of the glaze. In fact, investigators were for the most purposes practical, that is wanting a good result under certain required condition, and finding "cure" to faults. Many empirical rules have been formulated; only some of these are quite useful.

Large numbers of very small crystals have opacifying effect due to their large surface area for the reflectance provided. C.W. Parmelee and W. Horak (2) worked on "the microstructure of some raw lead glazes" and concluded that zinc oxide must not be used in quantities larger than O.3 equivalents as zinc silicate might then crystallize out in large crystals. Titania must be used with care as even if introduced pure it very easily forms yellow stains with any iron impurity (3).

In a basic melt containing an excess of zinc oxide, zinc-silicate is the precipitate. Other crystals are formed in basic melts but the mechanism of their formation and what crystals these are is still a source of controversy.

Purdy and Krehbie (4) found that manganese oxide had the greatest crystallizing tendency, producing large and varied crystals. Zinc oxide gives large crystals in certain areas. Titania produces small but evenly distributed crystals. They found that Na is more conducive to crystal formation than K. Colouring agents are usually taken up by the crystals or the vitreous phase and so can produce very fine effects (5). Norton showed that a growing period of an hour at fixed temperature lower than the maturing temperature of the glaze could produce crystal growth. He also showed that growth periods at different temperatures produced different crystal types. The kiln atmosphere throughout the firing should be oxidizing. Haldeman (6) reported the substitution of LiO_2 for Na was detrimental for large crystal formation but did form excellent mattes. Binn [7] observed that multicomponent glazes give better mattes. Parmelee stated that increase in Na_2O increases the number of crystals formed. The function of alkalies is to reduce viscosity and also assist crystallization.

Compounding of crystalline glazes still follows Seger's classification of batches chemically by equivalents of RO, R_2O_3, and RO_2. On the whole, however, the various components do have some kind of effect on solution of the glaze. A component may decrease or increase solubility, viscosity, vapour pressure, surface tension and possibly other characteristics of the solution. An increase in a component can increase the volume of the melt thereby decreasing the concentration of some constituents. A component which does not melt presents quite a different phenomena in the melt or system. Evaluation of the effect of components depends on theoretical study as well as experimental knowledge.

EXPERIMENTAL PROCEDURE

Several glaze trials were made and only one was chosen by the author as suitable for a thorough investigation. A suitable body was also prepared on which this glaze was applied.

Table I shows the composition of the glaze; Table II shows the chemical analysis of raw materials, and calculated mineral oxide constituents in the glaze (gms/100 gms batch) is shown in Table III. Weight percent oxides and empirical formulae are shown in Tables IV and V respectively.

TABLE 1

COMPOSITION OF GLAZE

Batch Wt. precent	Raw material
23	Kingman Feldspar
23	Nepheline Syenite
9	Whiting
28	Zinc Oxide
4	Rutile
13	Flint (Ground Ottawa)

TABLE II

CHEMICAL ANALYSIS OF RAW MATERIALS

	$Si0_2$	Al_20_3	Fe_20_3	$Ti0_2$	$Ca0$	$Mg0$	Na_20	K_20
Kingman Feldspar	66.5	18.4	.08		0.01		2.7	12.0
Nepheline Syenite	66.0	24.0	0.08		0.6	0.1	10.0	4.3
Whiting	1		0.5		54	2		
Flint (Ground Ottawa)	99.61	0.16	0.2		0.05	0.03		

The batches were weighed and each one was ball-milled for 30 minutes. Before milling one of the batches has 2 grams Co_2O_3 added and the other has 4 grams CuO added to it; these additions were made to effect colour or beauty in the glaze

Test bars were made from the body composition

TABLE III
MINERAL OXIDE CONSTITUENT IN GLAZE
(gms/100 gms batch)

	$Si0_2$	Al_20_3	Fe_20_3	$Ti0_2$	$Ca0$	$Mg0$	Na_20	K_20	$Zn0$
Kingman Feldspar	15.3	4.23						2.76	
Nepheline Syenite	15.1	5.5					2.3	1-	
Flint (Ground Ottawa)	13								
Whiting					4.86				
Rutile				4					
Zinc Oxide									28
Total	43.4	9.73		4	4.86		2.3	3.76	28

TABLE IV

Wt % Oxide in Glaze

K_20	3. 92
Na_20	2.39
$Ca0$	5.05
Al_20_3	10.13
$Si0_2$	45.19
$Ti0_2$	4.17
$Zn0$	29.15

TABLE V

FJORMULA OF GLAZE

0.042 K_20
0.039 Ma_20 0.753 $Si02$
0.099 Al_20_3
0.090 $Ca0$ 0.053 $Ti0_2$
0.360 $Zn0$

or

0.08 K_20
0.07 Na_20 1.42 $Si0_2$
0.19 Al_20_3
0.17 $Ca0$ 0.10 $Ti0_2$

TABLE VI
COMPOSITION OF PROCELAIN BODY

Raw material	Wt. %
Kingman Feldspar	30
Ajax P Kaolin (fine)	20
Velvacast Kaoline (coarse)	25
Flint (Ground Ottawa)	25

shown in Table VI. The bars were extruded with 1/4" x 1" cross section and 11" long; They were bisque fired to 1040 C. In this condition they were porous to take the glaze.

The glaze was adjusted to specific gravity of 1.4 and had pH of 8 and was applied to the bars by dipping. The sides of the bar were wiped after dipping leaving the glaze on one flat surface.

Furnaces used during the whole firing process were a Stone Temperature Gradient furnace Model TG-DA No. 155 and a small globar laboratory kiln. The wall of this latter kiln is constructed of 2-1/2 inches of G28 (2800 F) insulated firebrick (I.F.B.) backed up with 4-1/2 inches of G23 (2300 F) I.F.B. It has 10" X 12" silicon carbide setting but supported by posts out from 99% $A1_2O_3$ brick. The kiln is heated by 8 Hot Rods (silicon carbide heating elements), 1" diameter x 12" heating length x 29" overall length. These elements are wired as four parallel pairs in series, thus giving twice the nominal resistance of one element (0.61 ohms) or 1.22 ohms. The power supply is a 3-bank Powerstat, rated at 20 KVA or 84 amperes 240 volts wired into a 21 KVA stepdown transformer 240 V to 168 V and then to the kiln. The eight heating elements have a total rediation surface of 302 square inches.

The firing rate in the kiln was controlled by the use of the variable transformer (Powerstat). The temperature was measured with Pt - Pt + 13% Rh thermocouple and was controlled by a Wheelco galvanometer type on-off controller actuating a relay in the power circuit. The firing schedule for this kiln is shown in Figure 4.

The crystals resulting from various heat treatments were observed in a stereo binocular microscope and photographed using Richert Mettalographed and a Canon 35mm reflex camera. X-ray diffraction analysis was carried out on a Norelco diffractometer using Cuka radiation.

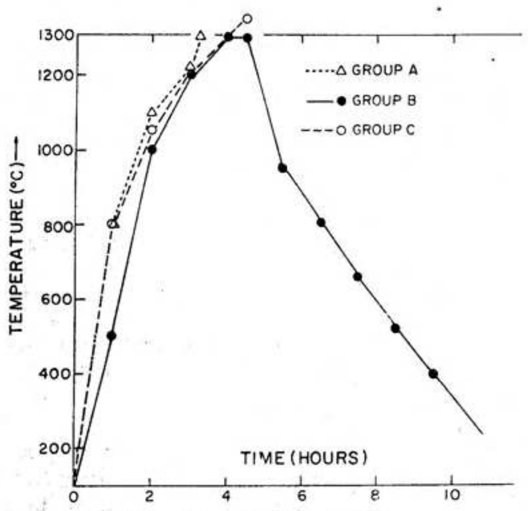

Figure 4 Firing Schedule of Glazed Bars

RESULTS AND DISCUSSION

In order to study the melting temperature and crystallization range of the glaze, a couple of bars were glazed and placed in the thermal gradient furnace and fixed at 1300°C. Examination of the bars after firing showed that this glaze has a melting point at 1250°C. Below 1200°C region of the bars the glaze appeared matte. Visible, blue fanklike willemite crystals appeared above the 1200°C region of the bar.

Having determined that the glaze matured and that crystals appeared between 1200°and 1300°C, uniform temperature firing tests were carried out in the globar kiln at various temperatures. Several bars were glazed and fired in this kiln :

A first set of bars (Group A) was fired at 1300°C without soaking. A second set of bars (Group B) was fired to 1300°C with 30 minutes soaking. A third set (Group C) was fired to 1350°C without soaking.

All tiles were allowed to cool to room temperature in the kiln where the cooling rate is essentially the same for all firings.

The various firing processes produced very interesting results. Bars fired at 1300°C (Group A) produced a cluster of round yellow crystal covering the whole surface of the bars. Viewed under binocular microscope the crystals were found to have a dark blue background. All crystals were macroscopic ; their identification and method of identification shall be discussed later. Bars fired at 1300°C with 30 minutes' soaking (Group B) has much more round gold crystals than that of Group A. In this group, however, the size of the gold crystals became reduced. Under the binocular microscope dark blue patches were seen touching the edges of the gold crystals. All these gold and dark blue patches have a light blue background. At 1350°C the number of the gold crystals increased considerably and their sizes became smallest. The round dark blue patches observed in Group B became bigger in size; much of the light blue background described in Group B has been taken up by the dark blue areas. The gold crystals have perceptible roughness to the touch.

The results showed that the higher the temperature, the greater the number of smaller crystals produced. On the whole, however, the firings of Group B and C have much better aesthetic qualities than Group A. As will be shown later, the yellow crystals are not present at temperature above 1100°C so the difference observed here may be caused by differences in cooling conditions rather than the maximum heat treatment conditions.

Cooling the kiln rapidly from 1300°C to 1100°C for 30 minutes, raising the temperature by 50°C for 30 minutes and allowing the kiln to cool to room temperature produced a cluster of large fanlike nature of the willemite crystals. Cooling the kiln to a temperature above 1100°C destroyed this visible fanlike nature of the willemite crystals. The author is convinced from this result that temperatures above 1150°C are inimical to the growth of any visible fanlike willemite crystal if needed.

Since the author's greatest interest was in the production of the gold crystals already mentioned, much attention was drawn to their study, when they occur during the firing process and what type of crystals they are. Glaze bars were fired at 1250°C, 1300°C and 1350°C. Each bar was allowed a soaking period of 30 minutes and then quenched at the temperatures mentioned. Another bar was fired in the globar kiln to 1350°C, soaked for 2 hours and then quenched. The draw trials from this experiment showed no gold crystals. Another group of bars were fired to 1300°C, and draw trials made at 1300° C, 1250°C, and a bar was left to cool to to room temperature in the kiln ; the draw trials at these various temperature also exhibited no gold crystal. However, the bar that was allowed to cool to room temperature in the kiln showed numerous round gold crystals covering the surface of the bar; the bar very much looked like the sample from Group A. With continued draw trials, the gold crystals begin to show only at 1100°C and below the surface of the glaze. Viewed under binocular microscope each yellow crystal appeared to be very much like little stars in concentric circles. At 1075°C the yellow crystals begin to show more clearly; this shows that the crystals were gradually coming out to the surface of the glaze. The binocular microscope did not show little stars in concentric circles at this time, but just round solid gold crystals. At 1050°C the round gold crystals showed much more clearly with few scattered willemite crystals. At

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