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Mixed Crystallisation Modes in Glass-Ceramic Enamel

DOUGLAS M. MATTOX
Ceramics and Glasses, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, USA

The crystallisation of a glass-ceramic enamel system in which two modes of crystallisation are observed is described in some detail. During the coating fusion, uncontrolled, spontaneous devitrification of kalsilite occurs throughout the glass. In a post heat treatment process a controlled, intentionally nucleated crystallisation of the matrix occurs. The preferential diffusion of iron from the substrate, through the glassy phase of the biphasal system during fusion is observed. The implication of this behaviour on adherence is noted.

1. Introduction

Glass-ceramic processes are typically thought of as being characterised by the controlled crystallisation of glasses [1]. Glasses which crystallise rapidly are felt to lack ultimate utility because of irreproducibility and the poor mechanical properties of uncontrolled, exaggerated grain growth [2]. Efforts to cool such glasses fast enough to avoid spontaneous crystallisation ordinarily result in the destruction of the piece by the unrelieved buildup of thermal stress. Thus the occurrence of spontaneous crystallisation is carefully avoided in glass-ceramics, and is frequently felt to be the harbinger of an unworkable system.

While these generalisations are valid for bulk glass systems, they are not necessarily extendible to glass enamel practice. In glass enamelling the fusion process takes place in the viscosity temperature region where spontaneous crystallisation [3] is likely to occur; and unlike bulk samples, rapid cooling rates are not typically destructive to the specimen. In the development of glass-ceramic enamels, spontaneous crystallisation may not be avoidable and may coexist with a controlled, intentionally crystallised phase. It is the purpose of this paper to describe, in some detail, a glass-ceramic enamel system in which mixed modes of crystallisation were observed to occur, and to make some observations on the implication of this phenomenon on adherence.

TABLE I Glass-ceramic enamel formulation

Oxide (or RF)	Mol %	Wt %	Batch (gms)
Na_2O	8·73*	7·40*	154 Na_2CO_3
K_2O	8·22	10·59	188 K_2CO_3
LiF	2·78	0·99	12 LiF
CaO	11·78	9·04	195 $CaCO_3$
ZnO	6·04	6·94	84 ZnO
BaO	6·93	14·54	226 $BaCO_3$
Al_2O_3	6·97	9·73	180 $Al(OH)_3$
TiO_2	1·73	1·89	23 TiO_2
SiO_2	46·75	38·95	471 SiO_2
Co_3O_4	0·07	0·25	3·0 Co_3O_4

*Two place accuracy in composition is not implied but is necessary in computation of trace ingredients.

2. Experimental Procedure

2.1. Sample Preparation

The glass-ceramic enamel system used in this study was a modification of the basic system reported by Snell [4]. The composition of the glass is given in table I. The glass was melted from reagent grade batch materials in a kyanite crucible for 6 h at 1371 °C with frequent stirring. After the glass had achieved an acceptable level of homogeneity, a disk was poured and annealed and the remainder of the glass fritted in water. The dried, fritted glass was introduced into a porcelain mill with alumina balls. Water was added to the mill in a weight ratio of frit to water of 5:2; 0·5 wt % carboxymethyl-cellulose (based on the water) was added as a powder to the mill to serve as a binder. All ingredients were milled for 8 h. The contents of the mill were then screened through 100 mesh and stored in a polyethylene jar. The suspension was then aged for a day before coating was attempted.

The enamel substrate was the titanium-bearing low carbon steel known as Ti-Namel* steel. The Ti-Namel used in these experiments was passed through a typical commercial pickling and nickel flashing procedure as described by Andrews [3]. The linear coefficient of thermal expansion was measured from 100 to 800°C and determined to be $13{\cdot}9 \times 10^{-6}/°C$. The substrates were 0·038 in. thick.

The frit suspension was applied to 2 × 2 in. metal specimen by air spraying. Uniform and easily varied thicknesses could be achieved in this manner. The coated panels were first dried and then fired in a 899° C oven for 2 min, yielding 00.08 in thick coatings. The resulting coatings appeared as typical glass enamels. These coatings were converted from glass to ceramic by exposing the coated panels to the heating schedule shown in fig. 1. This heat treating schedule is not unique [2], but was entirely satisfactory for the conversion of the coating. Thermal expansion measurements were made on the bulk glass and crystallised specimens and are shown in fig. 2, indicating the substrate is not unduly stressed by the glass-ceramic conversion.

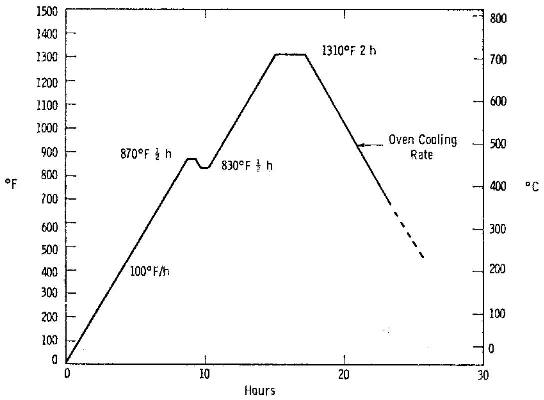

Figure 1 Heat-treating schedule for converting glass to ceramic.

2.2. Interface Characterisation

Samples of the coating before and after crystallisation were mounted, ground and polished perpendicular to the interface. To establish the distribution of elements in relation to the interface, X-ray line profiles were made perpendicular to the interface using a Materials Analysis Corporation, Model 400 electron beam microprobe. X-ray diffraction analyses were made of the fused and crystallised coating. Final characterisations were made by obtaining electron micrographs of the fused and crystallised coatings.

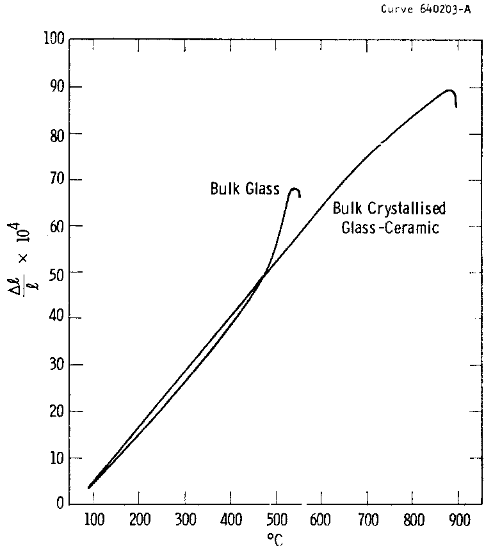

Figure 2 Thermal expansion curves of bulk and crystallised glass.

3. Results and Discussion

A typical ground and polished micrograph is shown in fig. 3. There was no significant difference in appearance between the fused and fused-crystallised coating and therefore a micrograph of the nonheat-treated coating is shown as representative. The interfacial roughening characteristic of many enamel systems [5] may be noted. The interfacial roughening did not undergo change during crystallisation. There was no evidence of dendrite formation.

The photomicrograph shown in fig. 3 was prepared subsequent to the microprobe scanning. The normal techique of depositing a thin conducting layer of graphite over the specimen was used; and, the micrograph is of a sample upon which this layer has been deposited. Accented by this deposition, optical microscopic examination revealed that texture had developed in the glass during fusion. Bulk glass samples examined in the same way gave no evidence of this inhomogeneity. This texture is evidenced

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*Trademark of Inland Steel Company.

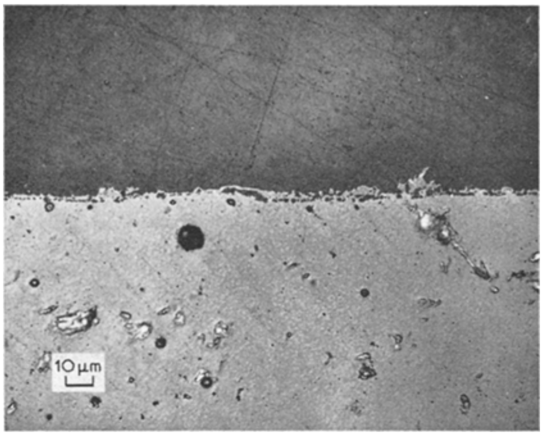

Figure 3 Metallograph of fused coating (light) on iron substrate (dark). Interfacial roughening can be observed and apparent absence of dendrites. Biphasal glass region is evidenced by grey on grey mottling.

in the glassy region by the grey on grey mottled appearance. Close examination of the micrograph reveals a uniformly distributed 2 to 4 µm sized phase surrounded by an interconnected, continuous phase.

Electron microprobe scans bore out the optical observation and indicated a high degree of phase separation. Because there are several phases present which are in the micron size range, and because these phases are in intimate intergrowth, it was not possible to determine the exact elemental associations by this technique.

Fig. 4 shows electron microprobe scans of those elements which tended to segregate in particular phases. Numerous line profiles and X-ray scanning micrographs were made of different areas to establish the trends indicated in this figure. The results of these studies indicated the presence of a potassium-alumino-silicate rich phase and a calcium-zinc-alumino-silicate rich phase, the interconnected continuous phase. Iron tended to preferentially diffuse through the calcium-zinc-alumino-silicate rich phase during the fusion process. Cobalt was uniformly dispersed through the glassy phase except for a concentration spike near the interface.

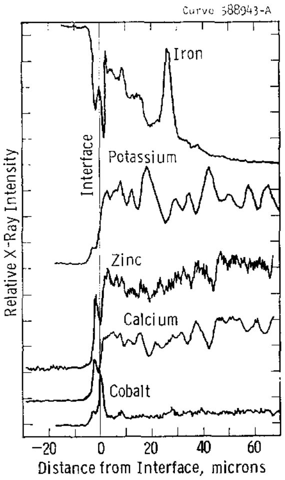

Figure 4 Relative elemental distributions perpendicular to interface as determined by electron microprobe scanning.

X-ray diffraction studies were undertaken of the fused coating and the fused, crystallised coating. The results indicated each to have kalsilite [6, 7] ($K_2O{\cdot}Al_2O_3{\cdot}2SiO_2$) present as the major phase. In the case of the nonheat-treated coating it was the only phase present. In the heat-treated sample, zinc aluminate ($ZnO{\cdot}Al_2O_3$) and a soda-lime-silicate crystalline phase ($2Na_2O{\cdot}CaO{\cdot}3SiO_2$) were also present with the remaining phase apparently an R_2O-BaO-SiO_2 glass.

A high degree of phase separation and crystal-

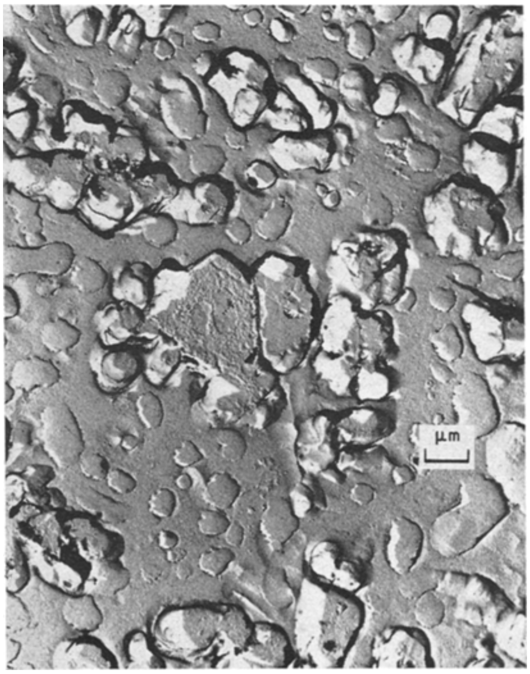

Figure 5 Electron micrograph of glassy region of fused coating. Spontaneously crystallised kalsilite phase is surrounded by glassy matrix.

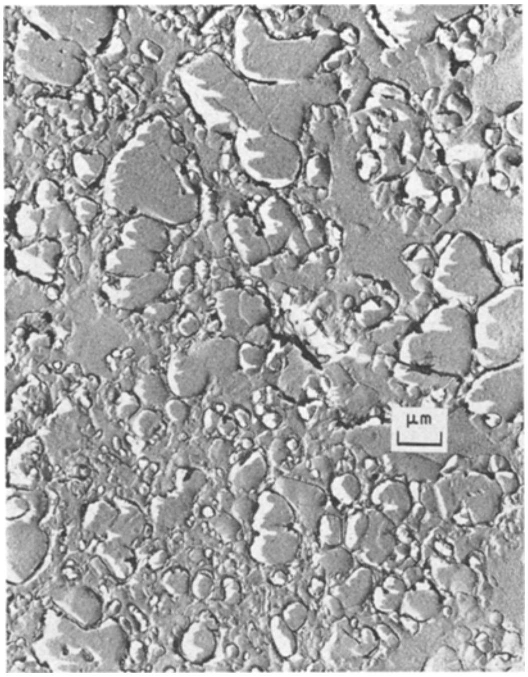

Figure 6 Electron micrograph of heat-treated coating. Matrix has undergone a uniform, fine-grained crystallisation. Average size of kalsilite crystals remains unchanged.

linity was indicated in the nonheat-treated coating. The possibility that this phase separation existed in the glass prior to enamelling was eliminated by X-ray and electron microprobe examination of the bulk glass. Electron microprobe studies of the fully crystallised coatings were made. The scans of these coatings showed no appreciable difference in the distribution of elements following crystallisation, except the iron tended to be more uniformly diffused through all phases.

To establish the role TiO_2 played in nucleating crystallisation in this system, a glass identical to the original composition was prepared, except that the TiO_2 was omitted. Coatings were made and studied by X-ray diffraction analysis. After application and fusion the kalsilite phase was evident. The coating was heat treated but no further crystallisation occurred as revealed by X-ray diffraction analysis.

As a final means of examination, electron micrographs of the original coatings were prepared. The samples were replicated with Parlodion using a PtC shadow at a 45° angle. Figs. 5 and 6 are the micrographs of the fused and fused, heat-treated coatings respectively. In fig. 5 the larger, spontaneously crystallised kalsilite crystals can be seen in a glassy matrix. Following heat treatment, the glassy matrix has crystallised extensively (fig. 6) at a much smaller and more uniform grain size, which is characteristic of controlled crystallisation. The average crystal size of what is presumed to be kalsilite remains unchanged, supporting the optical microscopic and the electron microprobe observations. There is still some glassy phase present in the heat treated, crystallised coating.

4. Conclusions

As an explanation of the unusual crystallisation behaviour of this system the following scheme is proposed. It seems that kalsilite freely precipitates from the glassy system at the temperatures and times of the coating fusion process. The presence of TiO_2 is not necessary for its nucleation since kalsilite crystallises in the absence of TiO_2. During the fusion process, iron from the substrate preferentially diffuses through the glassy phase due to the higher mobility of iron in the lower viscosity liquid phase, as contrasted with the effectively rigid kalsilite phase. Suppression of spontaneous crystallisation during fusion would improve adherence as a result of increased reactivity with the substrate. This implies that adherence, in enamel systems which undergo some crystallisation during fusion, is dependent on the time and temperature of fusion, since these will determine the glass-crystallising phase concentrations.

During heat treatment the matrix apparently crystallises under the influence of the nucleation catalyst, TiO_2. The crystallite size is much smaller than that of the kalsilite phase and cannot be resolved by electron microprobe. Small grain size is to be expected in cases of controlled, intentionally nucleated crystallisation. In conclusion a coating system has been described in which two modes of crystallisation occur; a spontaneous type which limits reactivity with the substrate and a controlled type which is intentionally nucleated.

Acknowledgements

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