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Phase Transitions in a Zirconia-Nucleated $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ Glass-Ceramic

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The complexity of the phase transformations occurring in glass-ceramic materials as a result of the time and temperature of heat treatment complicates investigations of material properties. A method of correlating the phase transformations with the time and temperature of heat treatment is presented in graphical form. A $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ composition nucleated with zirconia is used as a model.

1. Introduction

This paper presents a method of correlating the crystalline phase transitions occurring in a glass-ceramic material with the time and temperature of isothermal heat treatment. The method has proved to be very useful in understanding changes in physical properties associated with phase transformations. A zirconia nucleated $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ composition is used as a model. The correlation is presented as a time-temperature-transition (T-T-T) or isothermal transformation plot, often referred to as "C-curves" by metallurgists. To the writer's knowledge, detailed information of this type has not been presented in the literature for any glass-ceramic material. Van Vlack [1] has suggested that such relationships should exist and shows a hypothetical glass crystallisation "C-curve". Redwine and Conrad [2] discussed T-T-T plots but gave no detailed specific information.

2. Experimental

The glass was prepared from the purest available commercial materials with a total impurity content of approximately 0.5%. The analysed composition of the glass is: 50.16 SiO_2, 28.51 Al_2O_3, 10.92 MgO and 10.34 ZrO_2 by wt %. Approximately 15 lb (6.8 kg) of batch material was carefully blended and melted in a platinum crucible in a gas direct-fired crucible furnace. The melting time was 72 h at a temperature of 1650° C including 52 h of stirring and 12 h of fining. After fining the melt was drawn into a $\frac{1}{4}$ in. rod utilising a mechanical drawing process and a platinum plate with an orifice. The quench was controlled by the ambient temperature and the rate of draw. The rod was not annealed.

Samples approximately 2 in. long were cut from the rod and heat treated in Marshall tube furnaces with a control precision of $\pm$ 1° C. The samples were placed rapidly into the furnaces which were maintained at the desired heat treatment temperature. With this technique, practical heat treatments attain the closest approach to true isothermal conditions. After heat treating for the desired time, the samples were quenched out of the furnace and allowed to cool to room temperature.

Portions of the sample from each heat treatment were selected for microscopic examination and X-ray diffraction. The X-ray diffraction was performed on a high resolution Guinier powder camera. The resulting X-ray diffraction patterns were compared with ASTM data and literature values [3-5] in order to identify the phases present.

3. Results

Table I presents the time and temperature of heat treatment and phases identified for each of the samples. The table does not give a clear insight into the time and temperature association of the phase transitions. This association is shown advantageously by a plot of the time-temperature of phase transitions as given in fig. 1. The stress release line is determined by the strain point and annealing point and represents the time necessary to remove any residual stress from the glass. This line is of significance because it is closely associated with the lower temperature limits of

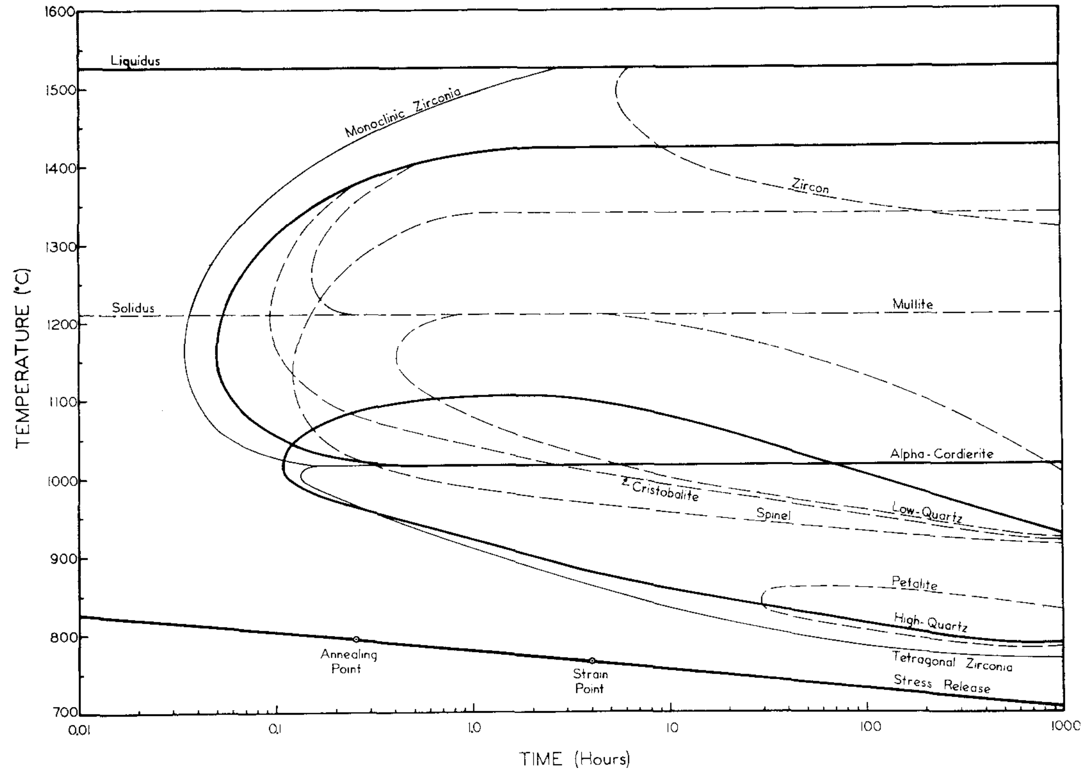

Figure 1 Phase transitions in the $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$ plus 10 wt % ZrO_2 glass-ceramic material.

nucleation in glass-ceramic systems. The second heavy line on the plot is the high-quartz solid solution line. This line represents the area within which the high-quartz solid solution is detectable in the X-ray diffraction pattern. The limit of detectability is probably somewhere under 5 % of the major phase and at the extreme limits of the area the strongest line of the phase is barely discernable in the diffraction patterns. The Guinier camera is particularly valuable in this type of study because relative intensities for a series of times at a given isotherm may be compared directly. The first appearance of a phase is quite easily detected in such a series. The next heavy line is the boundary of the α-cordierite phase which is the predominant phase during higher temperature and longer time of heat treatments. The next heavy line on the plot is the liquidus line above which no crystalline material exists.

Nucleation is accomplished in this material by the addition of zirconia which produces uniform internal nucleation. The mechanism of the nucleation by the zirconia has been discussed by Neilson [6]. The first zirconia phase observed is the stabilised tetragonal form which is very similar in *d*-spacings to published values for calcium oxide- or ceria-stabilised zirconia. (Minor phase transition boundaries are plotted as thin lines in fig. 1. Where complete data are lacking, dashed lines are used). At long times and low temperatures the next phase observed is a magnesium petalite phase which has been discussed by Holmquist [7]. After extended heat treatment of the high-quartz solid solution phase, spinel is detected in the diffraction patterns and probably represents an exolution of magnesium and aluminium from that structure because it is closely associated with a major shift in spacing and line intensities of the high-quartz phase to form a pattern comparable with low-quartz although both quartz phases coexist for considerable time and temperatures. Another phase encountered in this region is cristobalite which persists above the solidus temperature. Closely associated with the appearance of the α-cordierite, stabilising ions in the zirconia are exsolved, and the zirconia present above these temperatures quenches to the monoclinic form. The next line on the plot is the

TABLE I Phases formed versus heat treatment

Temperature	Time (Hours)	Phase assemblage	Temperature	Time (Hours)	Phase assemblage
791°C	24	G	838°C	4	G
	30	G		8	Z
	60	Z		10	Z
	100	Z		14	Z
	150	Z		20	Z
	200	Z		28	Z, HQ, P
	400	Z, P, HQ		40	HQ, Z, P
	(500)	Z (GS)		64	HQ, P, Z
	810	P, Z, HQ		100	HQ, P, Z
	(1000)	P, Z, HQ (GS)		150	HQ, P, Z
				(500)	HQ, P, Z (GS)
				(1000)	HQ, Z (GS)
903°C	1	G	977°C	8 min	G
	1¼	G		10 min	HQ
	1½	Z		12 min	HQ, Z
	1¾	Z		14 min	HQ, Z
	2	Z		1	HQ, Z
	2½	Z, HQ		2	HQ, Z, S
	3	HQ, Z		4	HQ, Z, S
	6	HQ, Z		7	HQ, Z, S
	12	HQ, Z		9	HQ, Z, S
	24	HQ, Z		12	HQ, Z, S
	48	HQ, Z		15	HQ, Z, S
	70	HQ, Z		20	HQ, S, Z
	90	HQ, Z		22	HQ, S, Z
	150	HQ, Z		30	HQ, S, Z, C
	200	HQ, Z		40	HQ, S, Z, C, LQ
	248	HQ, Z		79	HQ, S, Z, C, LQ
	290	HQ, Z		160	C, LQ, S, Z
1060°C	½	HQ, S, Zm, C, AC	1155°C	¼	S, Zm, AC, C, L
	¾	HQ, C, AC, Zm, S		½	S, Zm, LQ, AC, C, L
	1	HQ, C, AC, Zm, S		1	LQ, S, Zm, C, AC, L
	1½	HQ, C, AC, Zm, S		2	LQ, S, Zm, C, AC, L
	2	HQ, LQ, C, AC, Zm, S		4	LQ, C, S, Zm, AC, L
	3	HQ, LQ, C, AC, Zm, S		8	LQ, C, S, Zm, AC, L
	4	HQ, LQ, C, AC, Zm, S		16	C, LQ, Zm, S, AC, L
	5	HQ, LQ, C, AC, Zm, S		32	C, LQ, Zm, S, AC, L
1265°C	¼	AC, C, Zm, S, M, L	1394°C	3	AC, C, Zm, M, L
	½	AC, C, Zm, S, M, L		6	AC, C, Zm, M, L
	1	AC, C, Zm, S, M, L		12	AC, C, Zm, M, L
	2	AC, C, Zm, S, M, L		24	AC, C, Zm, M, Zir, L
	8	AC, C, Zm, S, M, L		48	AC, C, Zm, Zir, M, L
	16	AC, C, Zm, S, M, L			
	32	AC, C, Zm, S, M, L			

Key:

G – glass
HQ – high-quartz solid solution
LQ – low-quartz solid solution
Z – tetragonal zirconia solid solution
AC – alpha-cordierite
C – cristobalite
M – mullite
L – liquid
S – spinel
P – petalite
Zm – monoclinic zirconia
Zir – zircon
(GS) – gradient furnace sample

solidus above which the metastable phases are not observed. The phases present above the solidus are monoclinic zirconia, zircon, spinel, cristobalite, α-cordierite and glass. These are the equilibrium phases for this quaternary system as reported by Herold and Smothers [8]. The crystalline phases gradually disappear with increasing temperature above the solidus. Zircon is the last crystalline phase existing just below the liquidus at extended times. The monoclinic zirconia probably forms at lower temperatures encountered in the heat-up of the samples and would not be present in samples quenched to temperature from super-liquidus temperatures.

The writer has chosen to use phase names for the metastable solid solution phases encountered in the heat treatment of this composition which most closely resemble the typical structures of the materials.

As may be seen in either table I or fig. 1, as many as six crystalline phases may coexist, whereas the phase rule predicts only four crystalline phases in equilibrium for a quaternary system. This feature in itself demonstrates the metastability of many of the phases encountered and the slow-reaction kinetics of silicate sysems in general which is responsible for the overlap of the metastable phase fields.

4. Conclusions

The phase changes which occur in this composition as a result of heat treatment have been investigated and the results presented in tabular form as well as a phase transition plot. The boundaries of time and temperature for each phase are shown on the plot. The general shape of the time-temperature field of existence of a phase is similar to those reported in metal systems. The major difference between silicate systems and metal systems is the reaction rate which is much slower in silicate systems and permits metastable phases to coexist for considerable times and temperatures. These low reaction rates make it possible to form glasses from silicate melts with practical techniques of fabrication whereas metals can exist as glasses only with very special quench techniques [9]. The metastable phases exist only at low temperatures where the ion mobility is restricted as indicated by the high viscosity of the material. A metastable phase exists over time and temperature conditions which represent a completely closed area. In contrast, a true equilibrium phase exists to infinite time over a temperature range and, thus, has a truly open boundary of time and temperature. At temperatures above the solidus, high mobility exists because of the presence of a fluid residual glass phase and the equilibrium phases are produced.

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