Journal of the European Ceramic Society **8** (1991) 181–185

The Effect of Manganese Doping on the Mechanical Behavior of Cordierite Glass-Ceramics

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(Received 13 February 1991; accepted 22 April 1991)

Abstract

The effect of manganese doping on the mechanical properties of cordierite-based glass-ceramics series was investigated. The fracture toughness dependence on microstrain level of cordierite crystals was established. Two regions of increased fracture toughness were due to the crack front interactions with the microcracks and with the residual stress fields, respectively. The effect of doping on the thermal shock fracture resistance is associated with the decrease in the thermal coefficient of linear expansion of glass-ceramics.

Die Auswirkung einer Mangandotierung auf die mechanischen Eigenschaften wurde an einer Reihe von Glaskeramiken auf Cordieritbasis untersucht. Die Abhängigkeit der Bruchzähigkeit vom Spannungszustand der Cordieritkristalle konnte abgeleitet werden. Die beiden Bereiche erhöhter Bruchzähigkeit resultieren aus der Wechselwirkung der Rißfront mit den Mikrorissen und mit den zurückbleibenden Spannungsfeldern. Die Auswirkung der Dotierung auf die Thermoschockbeständigkeit wird mit der Abnahme des Wärmeausdehnungskoeffizienten der Glaskeramik korreliert.

On a étudié l'effet du dopage par le manganèse sur le propriétés mécaniques de vitro-céramiques à base de cordiérite. On a établi la relation entre la ténacité et le niveau de microcontraintes de cristaux de cordiérite. Les interactions du front de fissure avec, respectivement, les microfissures et les champs de contrainte résiduelle donnent naissance à deux régions de ténacité accrue. L'effet du dopage sur la résistance à la rupture par choc thermique est associé à la diminution du coefficient thermique d'expansion linéaire des vitro-céramiques.

1 Introduction

The glass-ceramics based on cordierite feature attractive mechanical properties, resist thermocyclic loading and can be employed as structural materials.[1,2] The structure of the cordierite-based glass-ceramics results from complicated phase transformations in the process of the matrix glass crystallization while the crystalline and residual glass phases differ considerably in their composition and properties. The relation of these properties, as well as the volume content and morphology of phases, determine the macroscopic properties of glass-ceramics. The desired characteristics of the cordierite phase and structure of the glass-ceramics can be ensured by means of doping.

It is well known that there is a comparatively wide range of solid solutions with cordierite structure formed during partial replacement of Mg^{2+} by Mn^{2+}.[3] Because of the existing difference in the ionic radii of magnesium and manganese, such replacement must affect the level of structural microstrain, thermal expansion and other characteristics of glass-ceramics. The purpose of this study was to investi-

Journal of the European Ceramic Society 0955-2219/91/$3.50

gate the effects of the partial replacement of magnesium by manganese on the mechanical properties and thermal shock fracture resistance of the cordierite-based glass-ceramics with a high crystalline phase content.

2 Experimental

The compositions of the glass-ceramics studied are specified in Table 1. The composition of material K was close to the stoichiometric composition of the cordierite. The glass-ceramics of series S-1 and S-2 differed from the composition of material K in that their silica content was higher. In the series M, S-1 and S-2 the magnesium was partially replaced by manganese. To provide for the catalyzed crystallization all the glasses were doped with titania, whose content was 15 wt% in excess of 100 wt%.

The glasses were melted in an oxidizing atmosphere in a gas furnace at a temperature of 1550°C maintained for 2 h. To ensure the crystallization of the glasses they were heated in an electric resistance furnace at a temperature of 1200°C for 2 h. After treatment the samples were cooled down together with the furnace.

The phase composition of the samples and the parameters of the cordierite lattice were determined by X-ray diffraction (DRON-3 diffractometer, monochromatized CuK_α radiation). The root-mean-square values of the microstrain of the cordierite crystals were estimated according to the shape of the diffractogram lines by the method of the fourth moments.[4] The diffractograms were taken with the goniometer turning at a rate of 1/8 deg/min. The shape of the lines was measured at a pitch of $9{\cdot}09 \times 10^{-4}$ rad. The microstrain measurement error was within 4%. Employed as the standard was beryl, which is a structural analog of the hexagonal cordierite.

Table 1. Compositions of parent glasses

Series	*Oxides content (mol%)*				
	SiO_2	MgO	Al_2O_3	MnO	GeO_2
K	55·6	22·2	22·2	—	—
M-1	55·6	18·9	22·2	3·3	—
M-2	55·6	16·7	22·2	5·6	—
M-3	55·6	11·1	22·2	11·1	—
M-4	55·6	7·8	22·2	14·4	—
M-5	55·6	5·6	22·2	16·7	—
S-1	58·0	21·0	21·0	—	—
S-1-M-3	58·0	10·5	21·0	10·5	—
S-1-M-5	58·0	5·2	21·0	15·8	—
S-2	60·0	20·0	20·0	—	—
S-1-M-3	60·0	10·0	20·0	10·0	—
S-2-M-5	60·0	5·0	20·0	15·0	—
M-3-G-1	52·8	11·1	22·2	11·1	2·8

The structure of the samples was investigated by means of optical and scanning electron microscopy. Fracture toughness, K_{Ic}, measurements were performed using two methods: (a) three-point bending test of prismatic cross-section specimens with a straight-side notch (the curvature radius of the notch tip was approximately 30 μm); (b) indentation with the Vickers pyramid into the polished surface of the specimen at a load of 500 N and measurement of the length of the crack running from the indentation corner. The values of K_{Ic} were calculated from the results of both tests with the help of the relationships generally employed.[5] The strength was estimated by three-point bending test of the square-section bar specimens. It was also necessary to estimate microhardness, H_μ, and microbrittleness, A, of the specimens.[6] The latter is indirectly characteristic of the material's fracture resistance. The values of H_μ and A were determined by indentation of the Vickers pyramid into the specimen surface at a load of 2 N. The value of A was calculated using the formula[6]

$$A = 4{\cdot}8P(1 + 2\mu)/(4d^2 + l^2)$$

where P is the indentation load, d is the indentation diagonal, l is the length of longest diagonal crack, and μ is Poisson's ratio. Characteristic of thermal shock fracture resistance, ΔT_c, was the critical temperature difference in the process of quenching into water of the prismatic 30 × 30 × 3 mm polished specimens heated to a specified temperature in an electric furnace. The value of ΔT_c corresponded to the moment of detecting the cracks on the surface of the specimen. Crack detection was performed on the polished surfaces of specimens using a dye penetrant (according to Soviet Standard GOST 11103-85).

The thermal coefficient of linear expansion was measured using a quartz dilatometer. The heating rate was 3 deg/min. The specimens used were 50 mm long with a cross-sectional area 5 × 5 mm. The measurement error was within 3%. The specimens were also subjected to differential thermal analysis.

3 Results

The results of the phase analysis of the samples indicate that cordierite is the main crystalline phase, while small amounts of rutile and magnesium aluminotitanate are also present. Some amounts of manganese titanate were identified in the specimens containing manganese. The crystalline phase content in the specimens amounted to about 90%, regardless of the composition of the glass-ceramics studied.

The differential thermal analysis revealed that the temperature of the exothermic peak of the cordierite crystallization in specimen K of stoichiometric composition was 1180°C, which decreased as the manganese content increased as follows:

Composition	M-1	M-2	M-3	M-4	M-5
Exothermic effect temperature (°C)	1130	1120	1120	1070	1070

A partial replacement magnesium by manganese results in a continuous change of cordierite lattice parameters; *a* increases and *c* decreases:

Composition	K	M-1	M-2	M-3	M-4	M-5
c/a ratio	0·958	0·954	0·951	0·942	0·942	0·938

The glass-ceramics based on solid solutions of cordierite have fragmentary structure with fragments of 20–30 μm comprising the conglomerates separated by glass-like interlayers. The electron microscope observations show that the crystals have dimensions from 0·5 to 1·0 μm (Fig. 1).

The values of fracture toughness obtained by means of different tests agree well with each other. Figure 2 illustrates the fracture toughness versus the relative manganese content. It is obvious that there is no correlation between fracture toughness and manganese oxide content. Since the quantity, morphology and size of the particles of the main crystalline phase in all glass-ceramics investigated were about the same, it was only natural to study the relationship between fracture toughness and the internal stresses. Illustrated in Fig. 3 is the relationship between the microstrain of the cordierite crystals in glass-ceramics and the relative manganese content. With the concentration of manganese increasing the microstrain has a general tendency to decrease.

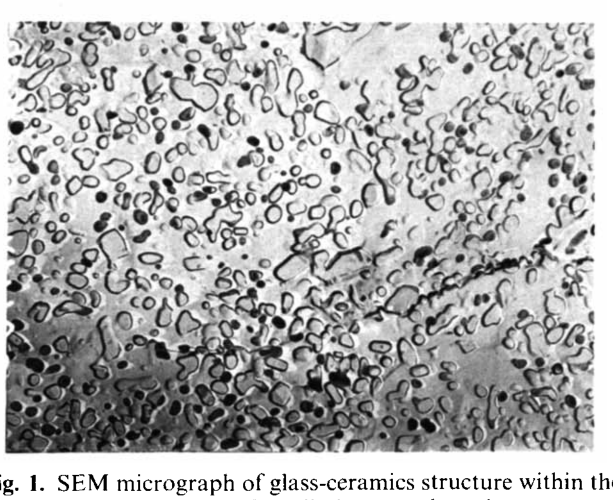

Fig. 1. SEM micrograph of glass-ceramics structure within the conglomerates of cordierite crystals region.

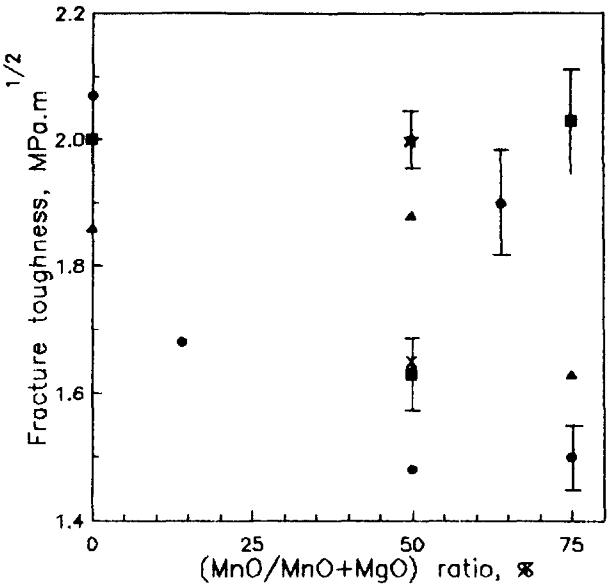

Fig. 2. Fracture toughness versus the relative manganese oxide content. Series: ●, K and M; ■, S-1; ▲, S-2; ×, M-3; ★, M-3-G-1.

The doping of cordierite with manganese also has a great effect on other properties of glass-ceramics. The data presented in Table 2 show that with increasing manganese content the microhardness, microbrittleness and thermal coefficient of expansion all decrease. The bending strength of the series S-1 and S-2 glass-ceramics also decreases, but for M compositions there is no correlation between ultimate bending strength and manganese content. However, doping with manganese results in an

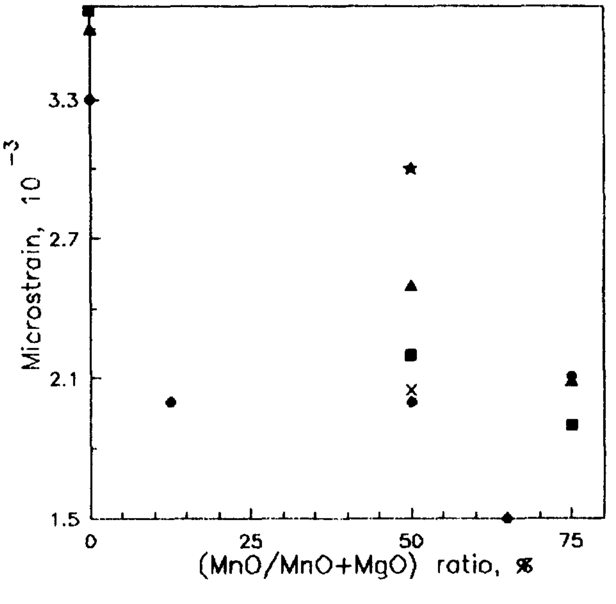

Fig. 3. Relationship between the microstrain of the cordierite crystals and the relative manganese oxide content. Series as in Fig. 2.

Table 2. Characteristics of glass-ceramics

Series	*d* (g/cm^3)	α (10^{-7} 1/K)	H_μ (GPa)	*A* (GPa)	σ (MPa)	ΔT_c (°C)
K	2·67	24	8·2	4·9	170	900
M-1	2·69	21	7·2	4·2	160	—
M-3	2·76	17	7·3	4·2	160	1 150
M-4	2·81	13	7·7	4·5	180	1 200
M-5	2·81	16	7·2	4·4	160	1 150
S-1	2·63	21	7·8	6·0	180	—
S-1-M-3	2·73	19	7·4	4·2	130	—
S-1-M-5	3·20	17	7·1	4·7	100	—
S-2	2·62	20	7·7	6·5	180	—
S-2-M-3	2·70	20	7·5	4·7	130	—
S-2-M-5	2·78	15	7·3	4·1	130	—
M-3-G-1	3·61	16	7·4	4·4	120	1 200

d = Density, α = thermal coefficient of linear expansion, H_μ = microhardness, *A* = microbrittleness, σ = ultimate bending strength, ΔT_c = thermal shock fracture resistance parameter.

increased thermal shock fracture resistance of the glass-ceramics.

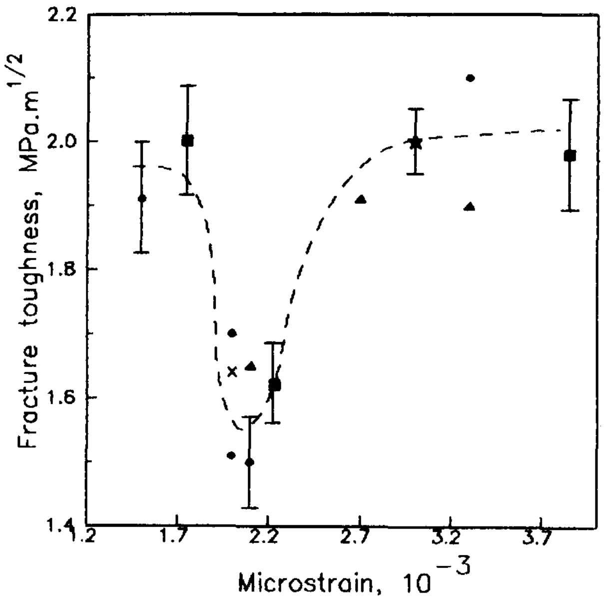

Fig. 4. Fracture toughness of glass-ceramics as a function of cordierite crystals microstrain level. Series as in Fig. 2.

4 Discussion

The principal merit of the cordierite glass-ceramics that determines their employment as promising structural materials is their resistance to strength degradation in conditions of thermal shock or thermal cyclic loading. The thermal shock fracture resistance of the brittle materials depends on (a) the level of thermal strain at given temperature gradients and conditions of heat exchange with the environment, and (b) the level of the mechanical properties that determine the resistance of the material to failure.

While increasing thermal shock fracture resistance, ΔT_c, on the one hand, the manganese content affects fracture toughness, strength and microbrittleness, which fact justifies the opinion that the thermal shock fracture resistance of the investigated materials is improved by the doping with manganese, as a result of the reduction of thermal expansion and, therefore, the thermal strain, $\alpha \Delta T$, where α is the thermal coefficient of linear expansion.

Any mechanical property of the investigated glass-ceramics, for example their fracture toughness, depends on many factors, such as phase composition, properties of phases and the thermal history of crystallization, which affect the residual stress level and distribution. The total effect is complex and results in an absence of correlation between such properties as fracture toughness and the composition of parent glass. Nevertheless, one of these effects may be dominant. For example, Fig. 4 shows the fracture toughness dependence on the microstrain level. There is a minimum corresponding to the microstrain $(1{\cdot}9\text{–}2{\cdot}3) \times 10^{-3}$. It may be assumed that at microstrain levels below the fracture toughness minimum toughening is the result of microcracking in the glass-ceramics structure. The increased microcracks density is confirmed in this region of fracture toughness–microstrain dependence by the luminescence measurement method. The effect of fracture toughness increase in microcracked structures is well known.[5] The rising part of fracture toughness–microstrain dependence with increasing microstrain level can be explained as a result of the interaction of the initial crack with the fields of internal residual stresses in the material structure. A model predicting similar effects has been developed.[7]

It follows that doping in the region of the solid solution formation with magnesium being partially replaced by manganese in the cordierite composition is efficient in increasing the thermal shock fracture resistance of glass-ceramics without causing considerable deterioration of their mechanical properties. It is advisable to introduce no more than 50% of manganese instead of magnesium, since a higher relative percentage of substitution has no practical effect on the properties of material.

5 Conclusions

The doping of the cordierite-based glass-ceramics with manganese, when magnesium becomes partially replaced by it, in the region of the formation of solid solutions with cordierite structure, makes the thermal shock fracture resistance of the cordierite-based glass-ceramics 250–300°C higher. The increased thermal shock fracture resistance is due to a reduction of the thermal coefficient of linear expansion, since doping with manganese has no effect on the increase in strength and fracture toughness. The increased manganese content makes the structural microstrain of the cordierite crystal lattice smaller. The dependence of fracture toughness on microstrain level has a minimum. The fracture toughness increase in the region of low microstrain level is due to microcracking and interaction of the crack tip with microcracks. The rising part of the fracture toughness–microstrain dependence can be explained as a result of crack interaction with residual stress fields. To ensure the optimum combination of properties it is advisable to keep the relative replacement of magnesium by manganese to within 50%.

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