JOURNAL OF MATERIALS SCIENCE 26 (1991) 3665–3669

Toughened glass-ceramics in the ZrO_2–Al_2O_3–SiO_2 system prepared by the sol–gel process

M. NOGAMI, K. NAGASAKA
Aichi Institute of Technology, 1247 Yakusa Toyota, 470-03 Japan

Monolithic glass-ceramics containing Al_2O_3 or TiO_2 were prepared in the ZrO_2–SiO_2 system by the sol–gel process from metal alkoxides. Tetragonal ZrO_2 was precipitated by heat treatment at 900–1200 °C and its crystal growth was increased by adding TiO_2 or Al_2O_3. Further heating at higher temperature resulted in the precipitation of zircon and monoclinic ZrO_2 which was transformed from tetragonal ZrO_2. The addition of Al_2O_3 had less effect on both the tetragonal-to-monoclinic ZrO_2 transformation and the precipitation of zircon. The fracture toughness increased as the size of tetragonal ZrO_2 particles increased and then decreased with the appearance of monoclinic ZrO_2 or zircon. The fracture toughness of the glass-ceramics was measured in the glass-forming regions of the ZrO_2–Al_2O_3–SiO_2 system. The fracture toughness was sensitively dependent on both Al_2O_3 and ZrO_2 content, of which the highest value achieved was ~ 9 MPa m$^{1/2}$ for the $50ZrO_2 \cdot 10Al_2O_3 \cdot 40SiO_2$ composition.

1. Introduction

Recently, a great deal of interest has been shown in ZrO_2-containing ceramics because of their high strength and fracture toughness. These properties have been attributed to a stress-induced transformation of tetragonal-to-monoclinic ZrO_2. This same ZrO_2-transformation toughening should be applicable to an amorphous material. Using the metal alkoxide sol–gel process, we have recently been successful in producing glass-ceramics in the ZrO_2–SiO_2 system containing up to 60 mol% ZrO_2 in which the tetragonal ZrO_2 crystals precipitated. The fracture toughness of these glass-ceramics increased as the size of the tetragonal ZrO_2 particles increased, reaching about 5 MPa m$^{1/2}$. However, on additional heating to transform tetragonal ZrO_2 into the monoclinic phase, an abrupt decrease in fracture toughness was observed.

In the present work, glass-ceramics containing TiO_2 or Al_2O_3 in the ZrO_2–SiO_2 system were prepared to increase fracture toughness of glass-ceramics. Monolithic gels, prepared by the sol–gel process, were densified and treated to crystallize and precipitate tetragonal ZrO_2. The fracture toughness was measured. High fracture toughness of glass-ceramics containing Al_2O_3 was investigated in relation to the crystalline phase and size of the tetragonal ZrO_2 crystal particles.

2. Experimental procedure

2.1. Preparation of glass and crystallization of ZrO_2

$Si(OC_2H_5)_4$, $Zr(OC_3H_7)_4$, $Al(OC_4H_9)_3$ and $Ti(OC_3H_7)_4$ supplied commercially were used as the starting materials. $Si(OC_2H_5)_4$ was first hydrolysed by dropping it into a mixture of H_2O, C_2H_5OH and HCl for which the molar ratio was maintained at 1:1:0.0027 mol per 1 mol $Si(OC_2H_5)_4$. After stirring this hydrolysed $Si(OC_2H_5)_4$ solution for 1 h, $Zr(OC_3H_7)_4$, $Al(OC_4H_9)_3$ or $Ti(OC_3H_7)_4$ was added, followed by stirring for an additional hour. The solution was poured into a teflon container which was then covered and left for 2–4 days to form a stiff gel with dimensions ~ 10 mm diameter and ~ 2 mm thickness. On gelling the solution, alkoxide was hydrolysed with water vapour in an atmosphere with relative humidity. However, this hydrolysis with water vapour was not adequate for complete hydrolysis of alkoxide. Owing to this incomplete hydrolysis, it was observed that the gel became black upon heating above 600 °C. In order to hydrolyse the alkoxide further, the gel was sealed with water in a vessel and then heated to 150 °C and held for 15 h. The resulting gel was heated at a rate of 50 °C h^{-1} and kept for 2 h at a fixed temperature. The crystallization heat treatment of these glasses was performed at temperatures between 1000 and 1300 °C.

2.2. Measurement of fracture toughness

Fracture toughness of glass-ceramics after the crystallization heat treatment was determined using the indentation fracture technique. Indentation tests were performed using a Vickers diamond pyramid with a microhardness tester at indentor loads of 5–15 N and a loading time of 15 s. Indent length and radial cracks extending from the corners were measured by an optical microscope approximately 1 min after the load was removed. The crack size, l, increased linearly with increasing load. It was also found that the crack-to-indent ratio, l/a, was < 2.5. Fracture toughness,

K_{Ic}, was calculated after Niihara *et al.* [4] using the following equation

$$[K_{Ic}\phi/(Ha^{1/2})]\,(H/E\phi)^{2/5} = 0.035(l/a)^{-1/2} \qquad (1)$$

where ϕ, H, a, E are the constraint factor (0.3), hardness, diagonal length of indentation and Young's modulus, respectively. H/E was determined by a Knoop indentation method, after Marshall *et al.* [5] using the following equation

$$b/a = 0.142\text{–}0.45(H/E) \qquad (2)$$

where b/a is the ratio of shorter and longer diagonal lengths of indentation.

2.3. Measurements of powder X-ray diffraction pattern and nitrogen gas adsorption isotherm

Crystals were characterized by powder X-ray diffractometry (XRD) using CuK_α radiation. The crystallite size of the tetragonal ZrO_2 particles was calculated by Scherrer's formula using the line broadening of the (1 0 1) diffraction line. The value of line broadening, defined as the line width at half-peak intensity, was obtained using Klug and Alexander's method [6] from the observed line broadening and an instrument broadening. The (1 0 1) diffraction line of α-quartz was used as the reference for the instrument broadening.

Specific surface area and pore volume measurements were made from the nitrogen gas adsorption isotherms at 77 K using a pore analysing system.

3. Results and discussion

3.1. Densification behaviour of monolithic gels

The gels treated with water vapour are porous containing physically and chemically adsorbed water on the gel particle surfaces. The specific surface area and pore volume are $\sim 300\ \mathrm{m^2\,g^{-1}}$ and $\sim 0.4\ \mathrm{cm^3\,g^{-1}}$, respectively, indicating that the gels consist of small particles having a diameter of few nanometres.

On heating the gels, they shrink according to the dehydration–condensation reaction and viscous flow sintering [7]. Fig. 1 shows the densification behaviour of a $50ZrO_2 \cdot 10Al_2O_3 \cdot 40SiO_2$ monolithic gel sample, in which a curve for moulded gel powder of the same composition is shown for comparison [8]. A gel powder has a low density ($\sim$ 1.5 $\mathrm{g\,cm^{-3}}$), making it necessary to heat it above 1200 °C for full densification. A monolithic gel can be densified at $\sim$ 900 °C by the viscous flow mechanism.

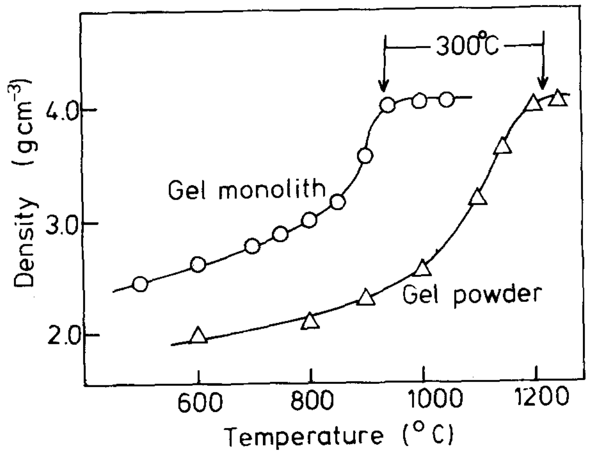

Figure 1 Densification curves of monolithic gel and moulded gel powder of the $50ZrO_2 \cdot 10Al_2O_3 \cdot 40SiO_2$ composition.

The fully densified glass body was transparent and an X-ray diffractogram did not show any crystals. It is worth noting that the densification temperature for a monolithic gel is 300 °C lower than for moulded gel powders.

3.2. Effect of TiO_2 or Al_2O_3 addition on the crystallization of glass

The crystallization behaviour of three different glasses, $50ZrO_2 \cdot 50SiO_2$, $50ZrO_2 \cdot 5TiO_2 \cdot 45SiO_2$ and $50ZrO_2 \cdot 5Al_2O_3 \cdot 45SiO_2$ was examined by differential thermal analyses and powder XRD measurements. The crystallization of amorphous glasses to tetragonal (t-) ZrO_2 began at $\sim$ 950 °C, which was a little higher than that for the densification of monolithic gels (Fig. 1). In the temperature range up to 1200 °C, the precipitating crystalline phase was only t-ZrO_2, of which the size increased as time and temperature increased. At 1200 °C or above, some crystals in addition to t-ZrO_2 were precipitated, which were sensitively dependent on the additive oxides. XRD patterns of the samples heated at 1200 °C and the size of t-ZrO_2 which was calculated from the peak width of the (1 1 0) diffraction line are shown in Figs 2 and 3, respectively. It has been reported that the growth of t-ZrO_2 in the amorphous silica matrix is controlled by the Ostwald ripening coarsening process and crystals larger than the critical size transform into monoclinic (m-)ZrO_2 during cooling [2, 3]. In our samples, the critical size for t- to m-ZrO_2 transformation was $\sim$ 50 nm (Fig. 3). The t- to m-ZrO_2 transformation was observed in the sample heated at 1200 °C for 20, 5 and 15 h for $50ZrO_2 \cdot 50SiO_2$, $50ZrO_2 \cdot 5TiO_2 \cdot 45SiO_2$ and $50ZrO_2 \cdot 5Al_2O_3 \cdot 45SiO_2$, respectively.

In the TiO_2 or Al_2O_3 containing sample, the t-ZrO_2 crystal grows much faster than in the silica matrix, and furthermore, the zircon($ZrO_2 \cdot SiO_2$) crystal precipitated together with ZrO_2 crystal (Fig. 2). The zircon crystal precipitates due to the reaction occurring between ZrO_2 crystal and amorphous SiO_2 under the coexistence of TiO_2 or Al_2O_3.

3.3. Fracture toughness of glass-ceramics

Fracture toughness, K_{Ic}, of the samples heated at 1200 °C is shown in Fig. 4 as a function of heating time. K_{Ic} increases nearly linearly with time, then passes through a maximum for TiO_2- or Al_2O_3-containing samples.

Generally, in ceramics containing t-ZrO_2, it is assumed that the stress concentration at the crack tips induces the t- to m-ZrO_2 transformation which increases the resistance to crack propagation. Therefore,

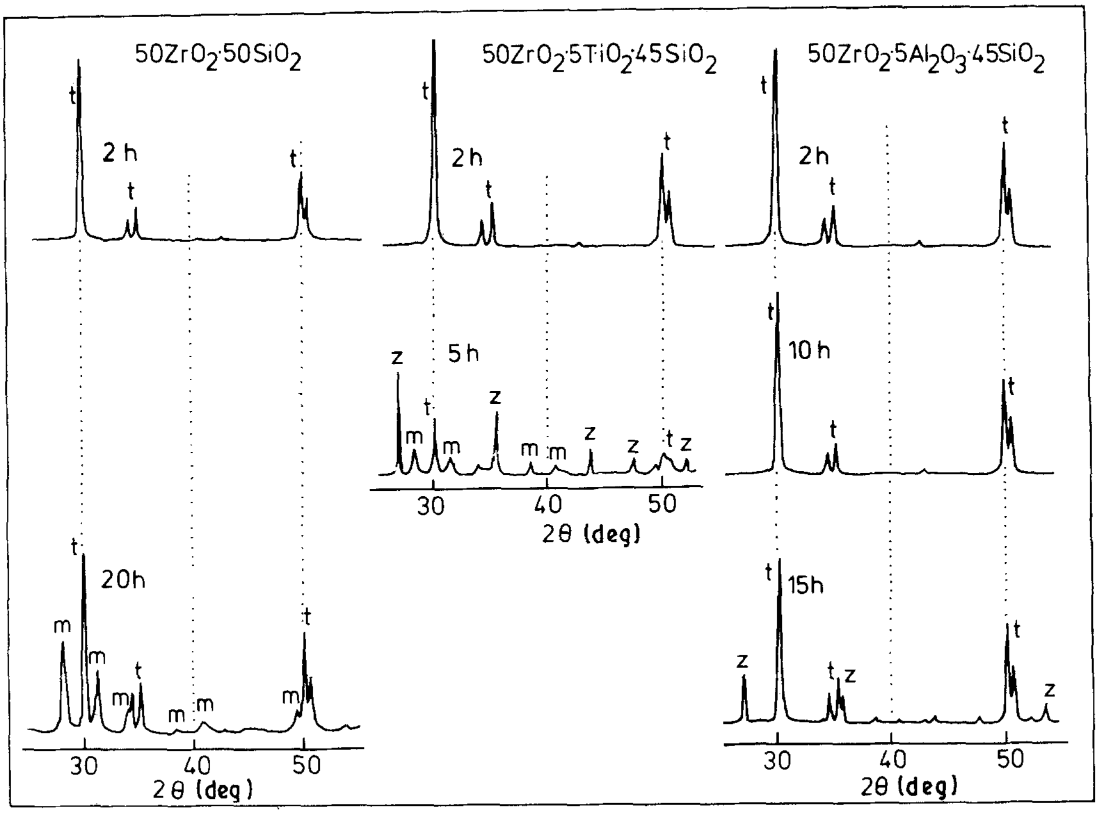

Figure 2 X-ray diffraction patterns of samples of the $50ZrO_2 \cdot 50SiO_2$, $50ZrO_2 \cdot 5TiO_2 \cdot 45SiO_2$ and $50ZrO_2 \cdot 5Al_2O_3 \cdot 45SiO_2$ compositions heated at 1200 °C at various times. t = $t\text{-}ZrO_2$, m = $m\text{-}ZrO_2$, z = zircon.

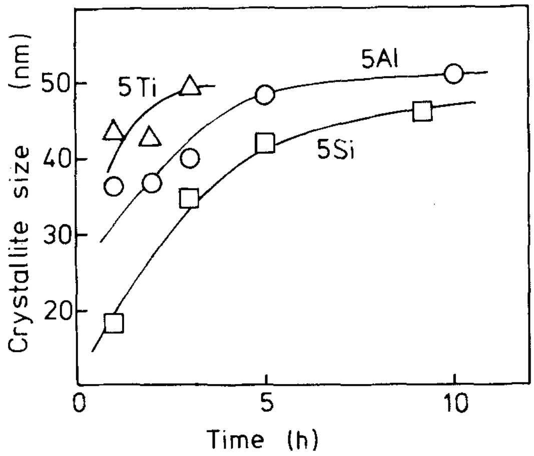

Figure 3 Isothermal growth of the $t\text{-}ZrO_2$ crystal in three different samples of the $50ZrO_2 \cdot 50SiO_2$ (5Si), $50ZrO_2 \cdot 5TiO_2 \cdot 45SiO_2$ (5Ti) and $50ZrO_2 \cdot 5Al_2O_3 \cdot 45SiO_2$ (5Al) compositions heated at 1200 °C.

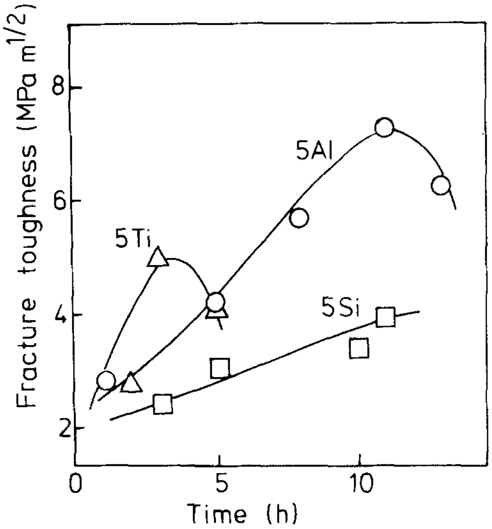

Figure 4 Relation between fracture toughness and heat-treatment time at 1200 °C of the glass-ceramics of the $50ZrO_2 \cdot 50SiO_2$ (5Si), $50ZrO_2 \cdot 5TiO_2 \cdot 45SiO_2$ (5Ti) and $50ZrO_2 \cdot 5Al_2O_3 \cdot 45SiO_2$ (5Al) compositions.

it is expected that K_{Ic} can be increased by precipitation and growth of $t\text{-}ZrO_2$ crystals. Furthermore, we found that K_{Ic} increased in proportion to the cube of the crystal size [1]. The present results for K_{Ic} (Fig. 4) agree with these concepts. K_{Ic} increases as the size of $t\text{-}ZrO_2$ increases, reaching a value of ~ 5 MPa m$^{1/2}$ at the ~ 50 nm size which is the critical size for the occurrence of the t- to $m\text{-}ZrO_2$ transformation. A higher K_{Ic} of TiO_2- and Al_2O_3- containing samples can be associated with a larger crystal size of $t\text{-}ZrO_2$ than in the silica matrix (Fig. 3).

In a sample of the $50ZrO_2 \cdot 5TiO_2 \cdot 45SiO_2$ composition, after reaching 5 MPa m$^{1/2}$, K_{Ic} decreases abruptly upon additional heating. These low K_{Ic} values are attributed to the existance of $m\text{-}ZrO_2$ or zircon crystal of which K_{Ic} is ~ 0.8 MPa m$^{1/2}$.

On the other hand, for the sample of the $50ZrO_2 \cdot 5Al_2O_3 \cdot 45SiO_2$ composition, $t\text{-}ZrO_2$ was observed to precipitate after growing to ~ 50 nm. The t- to $m\text{-}ZrO_2$ transformation and precipitation of zircon were observed after heating for longer than 13 h.

K_{Ic} increased with heating up to 10 h, reaching a value of 7 MPa m$^{1/2}$, which is much higher than those for the other two compositions.

3.4. Fracture toughness of glass-ceramics in the ZrO_2–Al_2O_3–SiO_2 system

The effect of Al_2O_3 on the K_{Ic} value of the glass-ceramics was examined over a wide range of composition in the ZrO_2–Al_2O_3–SiO_2 system. The examined composition ranges were 0–30 Al_2O_3, 30–60 ZrO_2 and 40–70 SiO_2 (mol %) as shown in Fig. 5.

Fig. 6 shows the XRD patterns of some of the samples in Fig. 5 heated at 1200 °C. The crystalline phases that precipitated are in agreement with the results of Low and Mcpherson [9] who studied the crystallization behaviour of the gel-derived ZrO_2–Al_2O_3–SiO_2 system. The first crystalline phase to appear at 950 °C was always t-ZrO_2 which grew and tranformed into m-ZrO_2 by heating for a long time at a high temperature. On further heating at these temperatures, zircon or mullite crystals were also detected, which are sensitively dependent on the gel composition, especially the Al_2O_3 content. K_{Ic} of the samples heated between 1100 and 1300 °C was measured. It was observed that K_{Ic} increased as the size of t-ZrO_2 increased and then decreased with the appearance of m-ZrO_2, zircon or mullite. The maximum value of K_{Ic} for each composition was achieved by choosing the heat-treatment time and temperature, as shown in Fig. 7 as a function of the ZrO_2 and Al_2O_3 content. It is apparent that K_{Ic} is sensitively dependent on the ZrO_2 and Al_2O_3 content. The Al_2O_3 content required to reach maximum K_{Ic} was lower for the glass-ceramics containing high ZrO_2. The highest K_{Ic} value (~ 9 MPa m$^{1/2}$) was obtained for a sample of the $50ZrO_2 \cdot 10Al_2O_3 \cdot 40SiO_2$ composition.

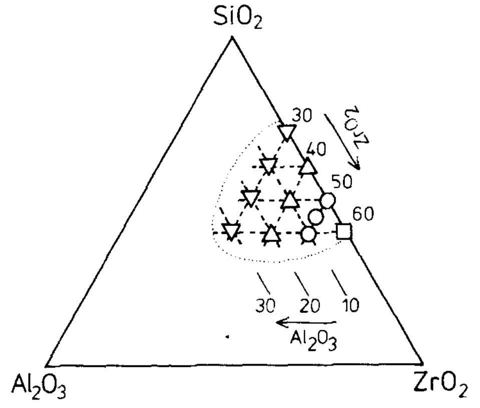

Figure 5 Compositions of glass-ceramics in the ZrO_2–Al_2O_3–SiO_2 system prepared in this study.

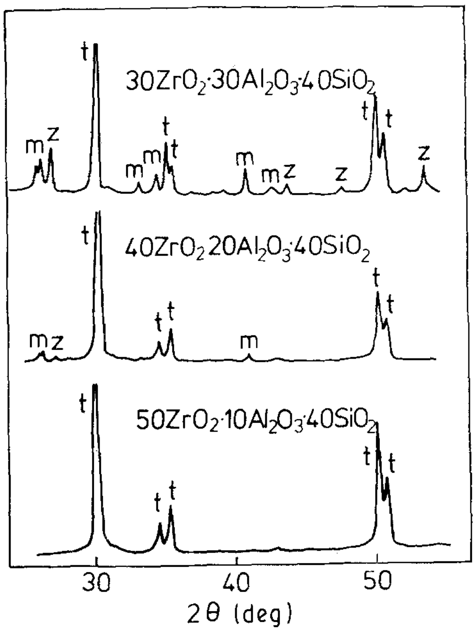

Figure 6 XRD patterns of samples containing various amounts of Al_2O_3 in the ZrO_2–Al_2O_3–SiO_2 system heated at 1200 °C at various times.

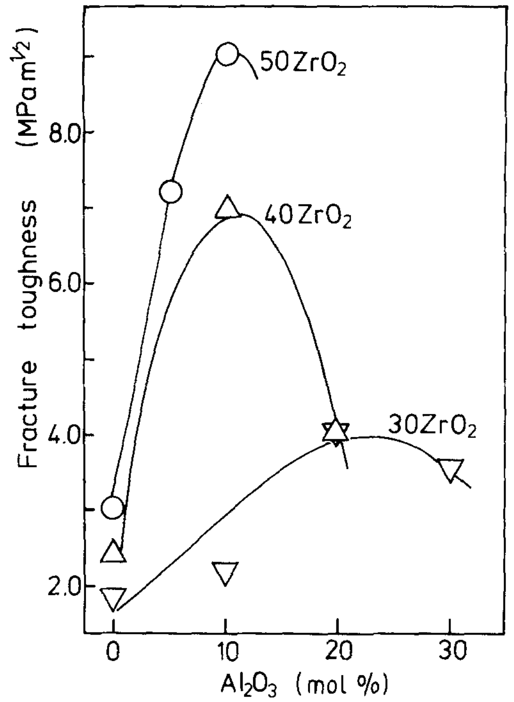

Figure 7 Relation between fracture toughness and content of ZrO_2 and Al_2O_3.

4. Conclusion

Monolithic gels containing Al_2O_3 or TiO_2 were prepared in the ZrO_2–SiO_2 system through hydrolysis of metal alkoxides. The monolithic gels were fully densified at ~ 900 °C, which was 300 °C lower than for moulded powders. Tetragonal ZrO_2 was precipitated by heat treatment at 900–1200 °C and its crystal growth was increased by adding TiO_2 or Al_2O_3. The fracture toughness increased as the size of the tetragonal ZrO_2 particles increased and then decreased with the appearance of monoclinic ZrO_2 or zircon. The fracture toughness was sensitively dependent on both the Al_2O_3 and ZrO_2 content, of which the highest value achieved was ~ 9 MPa m$^{1/2}$ for the $50ZrO_2 \cdot 10Al_2O_3 \cdot 40SiO_2$ composition.

Acknowledgement

This work was supported by a Grant from the Nippon Sheet Glass Foundation for Materials Science.

References

1. M. NOGAMI and M. TOMOZAWA, *J. Amer. Ceram. Soc.* **69** (1986) 99.

2. M. NOGAMI, *J. Mater. Sci.* **21** (1986) 3513.
3. *Idem, Yogyo-Kyokai-Shi* **95** (1987) 145.
4. K. NIIHARA, R. MORENA and D. P. H. HASSELMAN, *J. Mater. Sci. Lett.* **1** (1982) 13.
5. D. B. MARSHALL, T. NOMA and A. G. EVANS, *J. Amer. Ceram. Soc.* **65** (1982) 175.
6. A. P. KLUG and L. E. ALEXANDER, "X-ray Diffraction Procedures" (Wiley, New York, 1974) Ch. 9.
7. M. NOGAMI, *J. Non-Cryst. Solids* **69** (1985) 415.
8. M. NOGAMI, K. NAGASAKA, K. KADONO and T. KISHIMOTO, *ibid.* **100** (1988) 298.
9. I. M. LOW and R. MCPHERSON, *J. Mater. Sci.* **24** (1989) 1648.

Received 23 January
and accepted 19 November 1990