JOURNAL OF MATERIALS SCIENCE 21 (1986) 591–596

Hot pressing of Y_2O_3-stabilized ZrO_2 with Cr_2O_3 additions

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The sinterbility of Y_2O_3-stabilized zirconia with Cr_2O_3 additive was studied by a hot pressing technique using graphite and alumina dies; the dependence of the density on temperature, pressure and time was measured. Using graphite dies, it was found that the addition of Cr_2O_3 to Y_2O_3-stabilized zirconia was effective as an aid for densification due to formation of chromium at higher temperatures. Addition of Cr_2O_3 inhibited the grain growth of Y_2O_3-stability zirconia. The solubility of Cr_2O_3 in ZrO_2 was found to be 0.7 mol% at 1450° C. The results could be explained in relation to the phase relations of the system ZrO_2–Y_2O_3–Cr_2O_3.

1. Introduction

Materials formed from Y_2O_3-stabilized ZrO_2 (YSZ) with additions of Cr_2O_3 are potential conductors in MHD (magneto-hydro-dynamic) generators [1, 2] and in hydrogen production [3] or in other applications as zirconia-toughened ceramics [4]. Previously, we studied the phase relations in the system ZrO_2–Y_2O_3–Cr_2O_3 [5, 6] and found that Cr_2O_3 is compatible with ZrO_2 solid solution containing < 17 mol% Y_2O_3. In the case of sintering of materials in this system both Cr_2O_3 and stabilized ZrO_2 show poor sinterability. Cr_2O_3 is, in particular, less sinterable due to high volatilization at high temperatures and requires high temperatures (typically above 1600° C) in a reducing atmosphere to achieve high density [7]. However, such high temperatures cause excess grain growth of YSZ. Thus we decided to study the sinterability of the materials in this system by hot pressing.

Hot pressing of non-stabilized ZrO_2 has been reported by Samsonov *et al.* [8] and Chaklader and Baker [9]. Kainarskii *et al.* [10] studied the densification of ZrO_2 with various additives such as CaO, Y_2O_3, MgO, etc., and reported that the densification kinetics during the final stage of sintering were characteristic of diffusional sintering. Furthermore, they reported an optimum amount of additive above which the density of hot pressed specimens decreases. Specimens having densities of 99% for Sc_2O_3-stabilized and 97% for Y_2O_3-stabilized ZrO_2 have been reported by Evans [11] in hot pressing at 1500° C in creep studies. St-Jacques and Angers [12] also reported 99.5% densities for CaO-stabilized ZrO_2 by hot pressing at 1600° C. Kinoshita and Kose [13] also have reported the kinetics of hot pressing for CaO-stabilized ZrO_2. Wu and Brook [14] have reported MgO as a sintering additive for CaO- and Y_2O_3-stabilized ZrO_2 by hot pressing and zone sintering.

2. Experimental techniques

The sinterability of this system was studied by hot pressing 8 mol % Y_2O_3-stabilized ZrO_2 containing 0 to 3 mol % Cr_2O_3 and ZrO_2 stabilized by various Y_2O_3 contents, containing 1 mol % Cr_2O_3. Starting powders were prepared by coprecipitation from the solution mixtures of $ZrOCl_2$* (99.9%), $Y(NO_3)_3$† (99.99%) and $Cr(NO_3)_3$‡ (guaranteed reagent) with 6N NH_4OH [5, 6]. The coprecipitated gels were dried and calcined at 800° C for 17 h in an SiC furnace using a fused silica beaker. They were ground in an alumina ball mill with ethanol for 6 h to reduce agglomeration. After drying to remove all alcohol they were used for hot pressing studies.

The hot pressing equipment was based on a resistance furnace capable of reaching temperatures of up to 1700° C with $LaCrO_3$-based heating elements as shown in Fig. 1. The pressing atmosphere can be controlled by a gas flow or vacuum applied through an alumina protection tube. In the present study hot pressings were conducted using a graphite die in an argon atmosphere in the temperature range 1100 to 1500° C. The furnace was usually maintained at 650° C. The die filled with powder was loaded into the furnace at this temperature and total pressure was applied at that temperature. Then the temperature was elevated at a rate of 300° C h^{-1} up to the hot pressing temperature. After maintaining the system for the required period at the hot pressing temperature the pressure was released, then the system was cooled at the rate of 300° C h^{-1} to 650° C. A few hot pressings were done using an alumina die also in an argon atmosphere to study the effect of the die material. In

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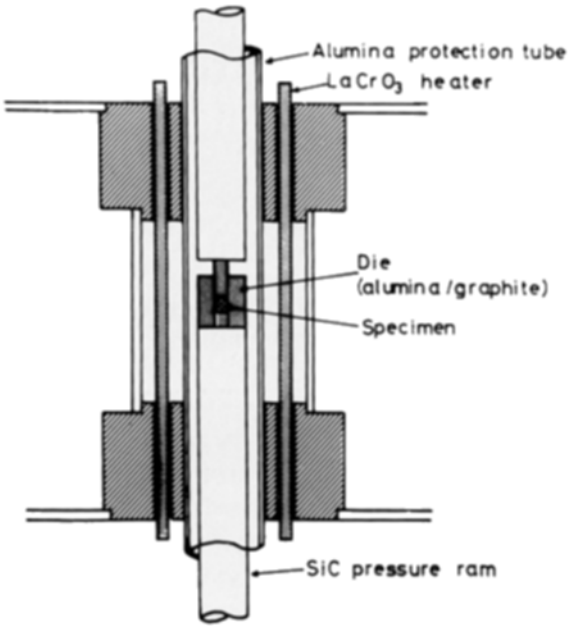


Figure 1 Schematic illustration of hot pressing equipment.

this case, molybdenum foils were placed between the punch and the sample to prevent the sticking of the specimen to the alumina punch through reaction.

The density of hot pressed specimens was measured by Archemedes' method in mercury. Microstructural observations were done for the polished and thermally etched (at 1550° C for 5 min) or chemically etched (in boiling H_3PO_4) surfaces and for the fracture surfaces using scanning electron microscopy (SEM).§ Phase identification and lattice parameter measurement of the hot pressed specimens were done by X-ray diffractomery.¶

3. Results

The densification of specimens was traced by the movement of the pressure ram during hot pressing under increasing temperature conditions. Shrinkage results for hot pressing, corrected for the expansion of the pressure ram and die are shown in Fig. 2. The shrinkage curves showed three stages of densification: a first stage with slowly increasing shrinkage rate; a second stage with shrinkage proportional to temperature; and a third with slowly decreasing shrinkage rate up to final density. The second stage with rapid densification for undoped YSZ started at about 850° C whereas in the case of Cr_2O_3-doped YSZ this stage started at a higher temperature, depending on the Cr_2O_3 content (at about 1000 and 1050° C for 1 and 3 mol % Cr_2O_3-doped YSZ, respectively). However, Cr_2O_3-doped YSZ showed rapid densification in the second stage and gave a greater shrinkage than that of undoped YSZ at the end of the second stage and above 1300° C.

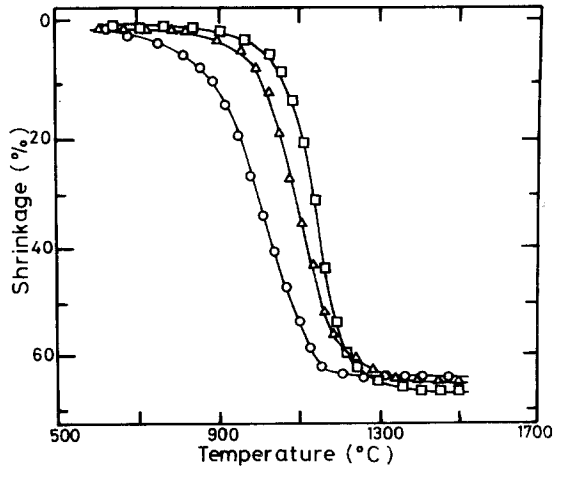


Figure 2 Shrinkage as a function of temperature for hot pressing of Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2, under 43.7 MPa pressure using a graphite die in increasing temperature. ○: 0% Cr_2O_3, △: 1% Cr_2O_3, □: 3% Cr_2O_3.

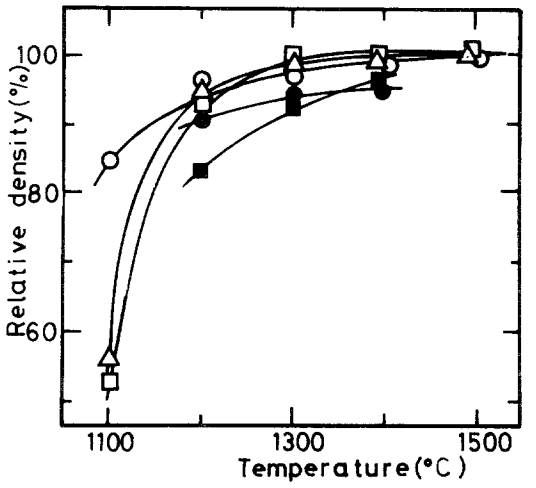


Figure 3 Density as a function of temperature for hot pressed Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2 (43.7 MPa, 30 min). Open symbols, graphite die filled symbols, alumina die. ○: 0% Cr_2O_3, △: 1% Cr_2O_3, □: 3% Cr_2O_3.

The specimens hot pressed in graphite dies were dark grey in colour due to carbon contamination from the die. Therefore the surface layer of each specimen was removed by grinding on a diamond disc, before making density measurements. The effect of temperature on hot pressing was examined for Cr_2O_3-doped YSZ (8 mol % Y_2O_3) between 1100 and 1500° C under 43.7 MPa pressure for 30 min. Fig. 3 shows the densities of the specimens hot pressed at various temperatures. Hot pressing in graphite dies showed higher densification for undoped YSZ than for Cr_2O_3-doped YSZ below 1200° C. Above 1200° C, however, Cr_2O_3-doped YSZ rapidly densified and at 1300° C acheived a density higher than pure YSZ. These results are consistent with the observation of pressure ram movement in Fig. 2. The results suggest that above 1200° C Cr_2O_3 enhances the densification of Y_2O_3-stabilized ZrO_2 on hot pressing in a graphite die. Hot pressing in alumina dies gave relatively lower densities for both pure and 3 mol % Cr_2O_3-doped YSZ (8 mol % Y_2O_3) materials. Furthermore it did not show clear evidence of any enhancement of the densification on Cr_2O_3 addition in contrast to the case of hot pressing in a graphite die.

The effects of pressure (Fig. 4) on hot pressing were

§JSM, T-200 Jeol, Tokyo, Japan.
¶RU-200 Rigaku Denki corporation, Todyo, Japan.

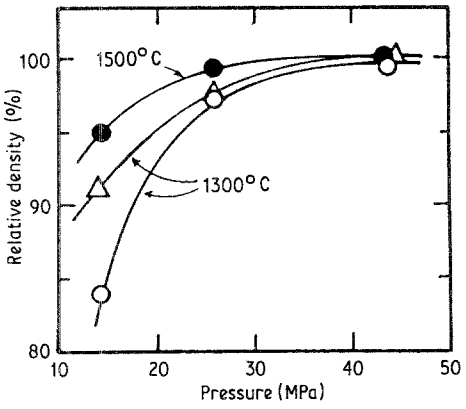


Figure 4 Density as a function of pressure for Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2 on hot pressing for 30 min. ○, ●: 1% Cr_2O_3, △: 3% Cr_2O_3.

examined using graphite dies at 1300 and 1500° C for 30 min. The use of low pressure caused a lower densification. However, hot pressing at higher temperatures, such as 1500° C, can yield 99% dense bodies at a pressure of 30 MPa. Again, by using a higher pressure of 43.7 MPa, fully dense bodies could be obtained even at a lower temperature of 1300° C. Densification with different hot pressing times was studied at 1200° C as shown in Fig. 5. Even at 1200° C fully dense bodies could be obtained by hot pressing 3 mol % Cr_2O_3-doped YSZ for 120 min. Microstructural observation of these specimens showed that grain growth with time was not so significant due to the low hot pressing temperature. Therefore hot pressing of Cr_2O_3-doped YSZ at a lower temperature, such as 1200° C, for a long time might be a good method to use to obtain a dense body with smalller grain size.

SEM observations of polished and chemically etched surfaces revealed secondary phase particles precipitated on the grain boundaries in both annealed (at 1200° C for 48 h) and unannealed specimens. As energy dispersive spectroscopy showed strong chromium lines at this secondary phase, it could be metallic chromium in the unannealed and Cr_2O_3 in the annealed specimens (see X-ray diffraction results). Typical microstructures of 0, 1 and 3 mol % Cr_2O_3-containing specimens hot pressed at 1500° C show Cr_2O_3 as a white phase among the dark ZrO_2 ss grains (in Fig. 6) after annealing. In some cases even intra-

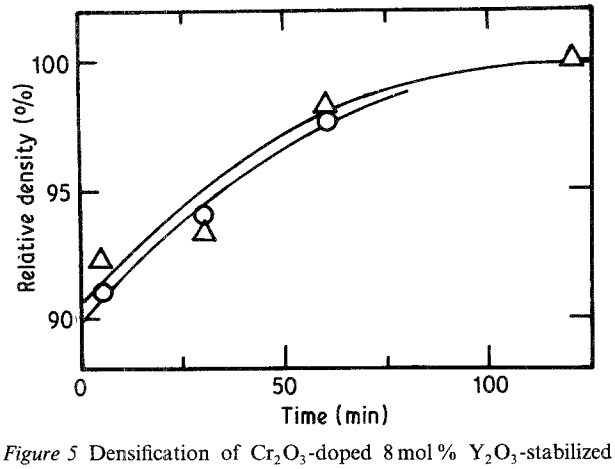


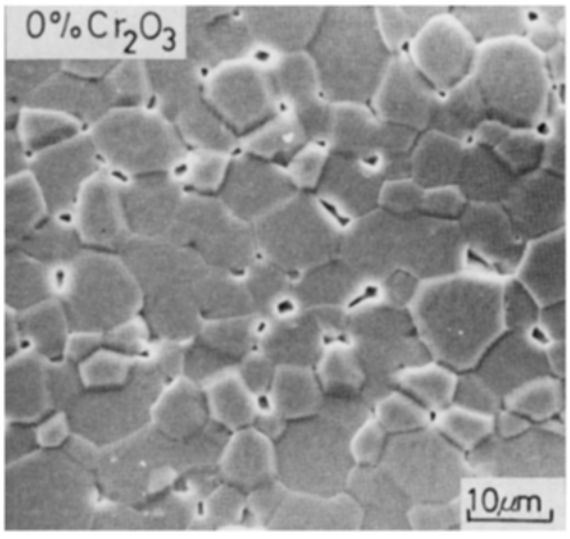
Figure 5 Densification of Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2 with hot pressing time at 1200° C under 43.7 MPa pressure. ○: 1% Cr_2O_3, △: 3% Cr_2O_3.

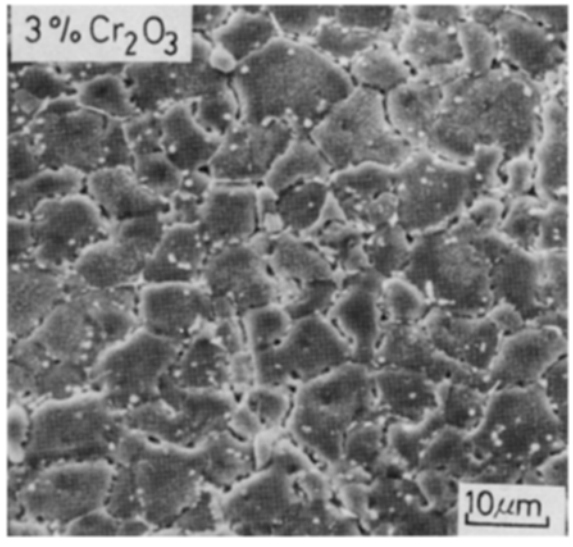
granaular particles could be seen, especially in the specimens hot pressed at higher temperatures. However, the microstructures showed a homogeneous Cr_2O_3 dispersion all over the specimen. As undissolved Cr_2O_3 could be seen in the specimens containing more than 1 mol % Cr_2O_3 the solubility of Cr_2O_3 in the ZrO_2 ss (8 mol % Y_2O_3) seems to be less than 1 mol %. Average grain sizes measured by the intercept method are shown as a function of the hot pressed temperature in Fig. 7. This shows smaller grain sizes for C_2O_3-doped YSZ than for pure YSZ specimens. Thus Cr_2O_3 seems to be a grain growth inhibitor in the Y_2O_3-stabilized ZrO_2.

A weight gain of 0.6% for 3 mol % Cr_2O_3-doped YSZ, hot pressed at 1500° C in a graphite die, was observed by annealing the specimens at 1200° C for 48 h in air. As a weight gain could not be observed for pure YSZ specimens, this was considered to be the oxidation of the metallic chromium produced during hot pressing in the graphite die. In order to check this directly, the specimens containing higher Cr_2O_3 contents (3 and 10 mol %) in 8 mol % Y_2O_3-stabilized ZrO_2 were hot pressed at 1500° C under 43.7 MPa pressure for 30 min and examined by X-ray diffraction of the contact region with the punch, and of cut and polished surfaces. The X-ray diffraction patterns for the 10 mol % Cr_2O_3-doped specimen (Fig. 8) showed that at the surface in contact with the punch, ZrO_2 has reacted with carbon to form ZrC. Since no chromium compound could be detected on the contact surface it was supposed that Cr_2O_3 also changed to carbide and dissolved in ZrC. On the polished section and the interior of the pellet, however, metallic chromium was observed instead of ZrC coexisting with cubic ZrO_2 ss. No Cr_2O_3 was detected even in the 10 mol % Cr_2O_3-doped specimen. However, on annealing at 1200° C for 24 h in air, X-ray diffraction showed the disappearance of chromium and the formation of Cr_2O_3 by oxidation of the chromium.

The lattice parameters were determined for 0, 0.3, 1 and 3 mol % Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2 specimens, hot pressed at 1300° C, after annealing them at 1450° C; the results are shown in Fig. 9. The lattice parameters for the specimens as-hot pressed at 1500° C and for the specimens annealed at 1450° C where almost identical. From these lattice parameter data the solubility of Cr_2O_3 in 8 mol % Y_2O_3-stabilized ZrO_2 is found to be 0.7 mol % Cr_2O_3 at 1450° C. This solubility limit is consistent with the microstructure observations also.

The sinterability of Cr_2O_3-doped ZrO_2 ss with Y_2O_3 in solid solution was studied by hot pressing 1 mol % Cr_2O_3-doped samples at 1200 and 1300° C. The relative densities are shown in Fig. 10 in comparison with the phase relations of the system ZrO_2–Y_2O_3–Cr_2O_3 [5, 6] at 1300° C. In the three-phase region of Cr_2O_3 + tetragonal ZrO_2 + cubic ZrO_2, 99% dense bodies could be obtained even at 1200° C by hot pressing for 30 min. In the phase regions containing fully stabilized ZrO_2, hot pressing gave low relative densities due to the low sinterability of cubic ZrO_2. However, a slight increase of relative density could be seen at 17 mol % Y_2O_3 which lies in the three-phase region of Cr_2O_3 +





cubic ZrO_2 + $YCrO_3$. Again in the cubic ZrO_2 + $YCrO_3$ two-phase region, relative densities decrease with increasing Y_2O_3 content. Thus it seems that the materials in the Cr_2O_3, cubic ZrO_2 and $YCrO_3$ three-phase region are the most sinterable of the cubic ZrO_2-containing materials.

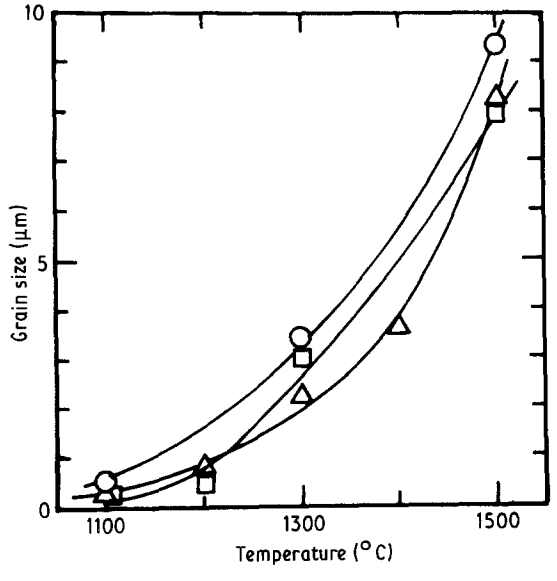


Figure 7 Average grain size plotted against hot-pressed temperature for Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2 (43.7 MPa, 30 min).

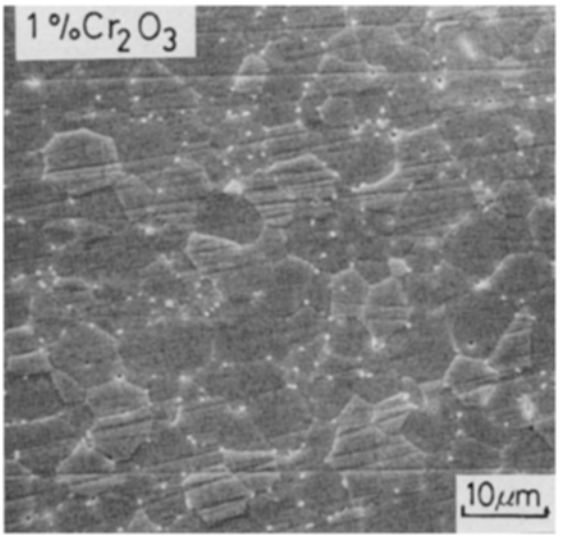


Figure 6 Microstructures of Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2 hot pressed at 1500° C under 43.7 MPa for 30 min, after annealing at 1200° C (etched in boiling H_3PO_4).

4. Discussion

In the present study, formation of metallic chromium was observed in specimens hot pressed in graphite dies. Yamaguchi [15] had studied densification of Cr_2O_3–ZrO_2 ceramics in reducing oxygen partial pressures and has reported that the densification of Cr_2O_3–ZrO_2 bodies occurs at 1500° C by the formation of chromium, Cr_3O_4 or off-stoichiometry oxide films on the surface of each particle. The reduction of Cr_2O_3 by carbon occurs through the reaction

$$\tfrac{2}{3}Cr_2O_3 + 2C \rightleftharpoons \tfrac{4}{3}Cr + 2CO$$

According to thermodynamic data [16] this reaction proceeds and reduction of Cr_2O_3 is favoured at temperatures above 1228° C. Thus above 1228° C the oxygen partial pressure in graphite dies becomes so low that Cr_2O_3 reduces to chromium; this has also been observed in the present hot pressing study.

Spriggs and Atteraas [17] and Spriggs [18] have described densification during hot pressing through the combine mechanisms of particle rearrangement, plastic flow and diffusion. Among these mechanisms particles rearrangment and plastic flow are the major contributing mechanisms in the initial stages and at low temperatures. Grain boundary sliding is one mechanistic process common to both plastic flow and particle rearrangement. Grain boundary sliding occurs by displacing one grain relative to its neighbour along their common interface due to shear stresses. In this case, a viscous or viscoelastic second phase at the grain boundary can low the deformation resistance and thus increase the rate of flow by grain boundary sliding. In hot pressing of Cr_2O_3-doped YSZ, this grain boundary sliding may be resisted by the non-viscous Cr_2O_3 secondary phase present at lower temperatures. Thereby densification of Cr_2O_3-doped YSZ is less than for pure YSZ at temperatures below 1200° C. However, above 1228° C, metallic chromium is formed on the grain boundaries by the reduction of Cr_2O_3. This easily deformable metallic chromium at

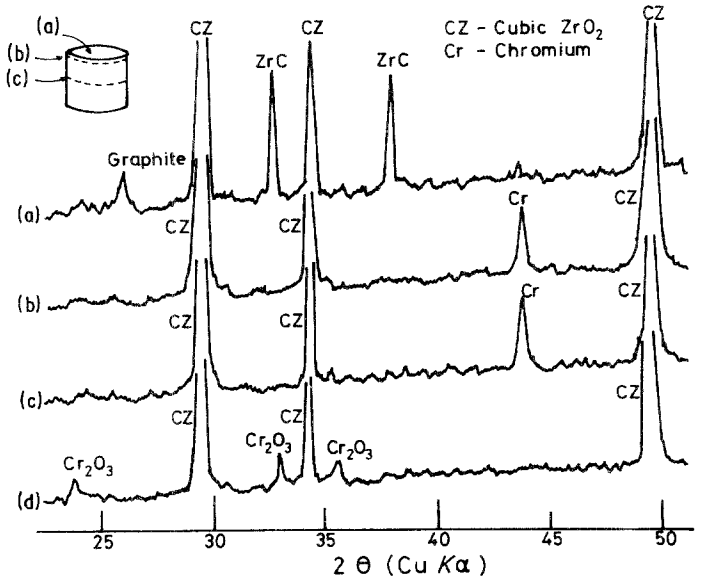


Figure 8 X-ray diffraction patterns of hot pressed 10 mol % Cr_2O_3-doped 8 mol % Y_2O_3-stabilized ZrO_2 specimen. (a) Surface in contact with punch, (b) polished surface, (c) centre, (d) centre after annealing.

the interfaces may accelerate the grain boundary sliding at higher temperatures similar to the higher deformation rates in press forging of nickel alloyed MgO [18].

Wu and Brook [14] reported that the densification of stabilized ZrO_2 was controlled by lattice diffusion, whereas grain growth at lower temperature was caused by surface diffusion. Even in hot pressing the applied stress directly assists the driving force for the densification process while leaving that for grain growth unaffected. Thus Cr_2O_3 dissolved in YSZ may reduce the surface diffusion of YSZ and inhibit grain growth in Cr_2O_3-doped YSZ during hot pressing. Consequently, the smaller grain size for Cr_2O_3-doped YSZ affects the densification rate. According to Coble's diffusion model [19] for hot pressing, the densification rate is proportional to r^{-2} (r = grain radius) for lattice diffusion-controlled hot pressing [20]. Thus smaller grain sizes in Cr_2O_3-doped YSZ can cause higher densification rates through diffusion in addition to grain boundary sliding.

The results of the hot pressing could be explained in relation with the phase relations of the system ZrO_2–Y_2O_3–Cr_2O_3 [5, 6]. Densification of the compositions lying in three-phase regions seems relatively higher than that of the compositions lying in the two-phase regions. A slightly higher density obtained for the Cr_2O_3-doped 17 mol % Y_2O_3 compsotion, coinciding with the apex of the Cr_2O_3 + cubic ZrO_2 + $YCrO_3$ three-phase region, seems to be a confirmation of the location of this apex.

5. Conclusions

1. At low temperatures (< 1200° C) Cr_2O_3 resisted initial stage densification occurring through particle rearrangement and plastic flow.

2. In hot pressing using graphite dies, Cr_2O_3 reduced to chromium at temperatures above 1200° C.

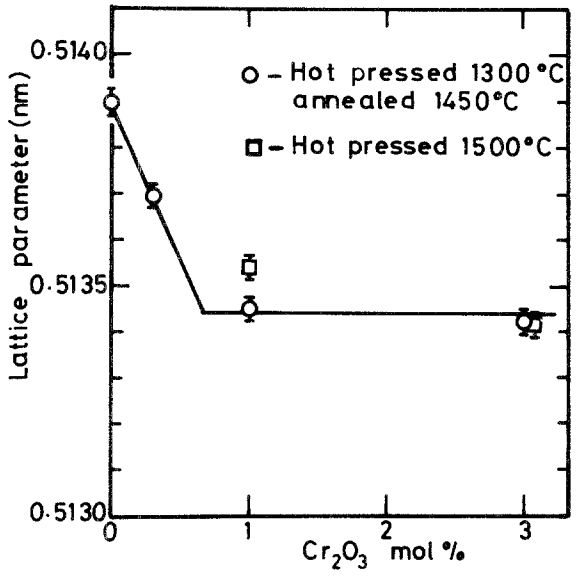


Figure 9 Lattice parameters in 8 mol % Y_2O_3-stabilized ZrO_2 as a function of added Cr_2O_3 content.

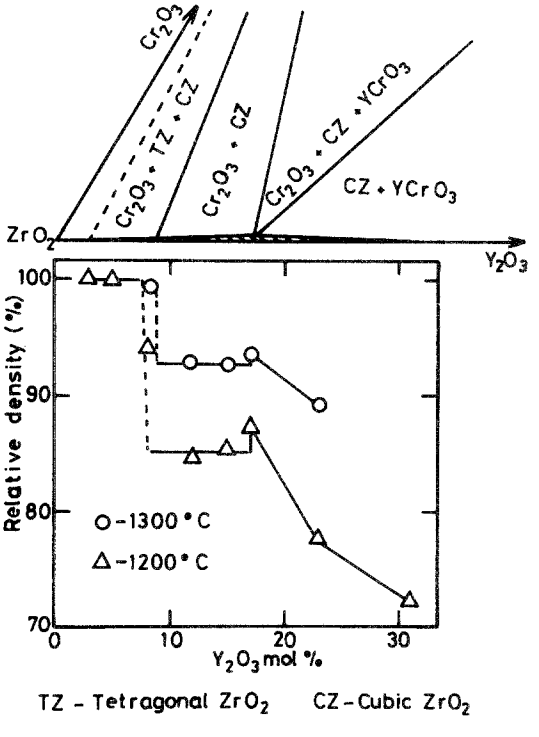


Figure 10 Relative density plotted against Y_2O_3 content for hot pressed 1 mol % Cr_2O_3-doped YSZ compared with the phase relations of the system ZrO_2–Y_2O_3–Cr_2–Cr_2O_3 at 1300° C. (43.7 MPa, 30 min, in graphite die.)

This chromium affects grain boundary sliding and densification occurs at higher temperatures.

3. The smaller grain sizes in Cr_2O_3-doped YSZ also have a positive effect on the densification occurring through diffusion.

4. The solubility of Cr_2O_3 in 8 mol % Y_2O_3-stabilized ZrO_2 was 0.7 mol % at 1450° C.

5. The variation of densification with Y_2O_3 content for Cr_2O_3-doped ZrO_2 ss was related to the phase relations of the system ZrO_2–Y_2O_3–Cr_2O_3.

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Received 27 November 1984
and accepted 29 March 1985