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Phase transformation in the Al_2O_3–ZrO_2 system

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Co-precipitation methods have been used to produce 20 mol % Al_2O_3–80 mol % ZrO_2 mixed oxides, from aqueous solutions of zirconium oxychloride and aluminium chloride, followed by precipitation with ammonia. The resulting gel was calcined at increasing temperatures, and X-ray diffraction confirmed that the structure remained amorphous up to 750 °C and then crystallized as a single-phase cubic zirconia solid solution, but with a reduced unit-cell dimension. At higher temperatures, the unit-cell dimension increased and, above 950 °C, this phase started to transform to a tetragonal zirconia (t-ZrO_2) phase, again of reduced cell dimensions compared with t-ZrO_2, with simultaneous appearance of small amounts of θ-Al_2O_3. Above 1100 °C, the tetragonal phase transformed to monoclinic zirconia on cooling, and the amount of θ-Al_2O_3 increased. Above 1200 °C, the θ-Al_2O_3 transformed to the stable α-Al_2O_3. These results confirm that aluminium acts as a stabilizing cation for zirconia up to temperatures of about 1100 °C. © *1998 Chapman & Hall*

1. Introduction

It is generally accepted that the solubility of alumina in the fluorite lattice of zirconia is low. For example Alper [1] reported that cubic zirconia (c-ZrO_2) solid solutions dissolve up to about 7 mol% Al_2O_3 at 1885 °C; Gevales [2] reported no evidence at all for the existence of such solid solutions. It has therefore been assumed that in materials such as zirconia-toughened alumina, made up of about 85 vol% Al_2O_3 and 15 vol% ZrO_2 the latter stabilized by (say) 3 mol% Y_2O_3, the alumina plays no part in the stabilization of the zirconia; this is done by the yttria alone. However, in some cases, it has been noted that the addition of alumina to zirconia-based materials does influence the microstructure and the properties, but this is believed to be due to the trace amounts of grain-boundary liquid generated [3]. However, recent work [4] has shown that alumina can stabilize the c-ZrO_2 and tetragonal zirconia (t-ZrO_2) when prepared at temperatures lower than those conventionally used for the sintering of alumina materials. In the latter work, samples were prepared by the alkoxide route, starting with mixtures of zirconium isopropoxide and aluminium isopropoxide dissolved in alcohol. After hydrolysis, it was shown that the temperature of crystallization gradually increased with increasing alumina content of the starting mix. Thus pure zirconia started to crystallize at 415 °C, and a 45 mol% Al_2O_3–55 mol% ZrO_2 mix crystallized at 835 °C; pure alumina was converted initially into an amorphous phase, which with increasing temperature changed to several defect alumina phases, finally transforming to α-Al_2O_3 at 1200 °C. X-ray diffraction analysis showed that below 1000 °C the Al_2O_3–ZrO_2 products were totally cubic in structure (with broadened peaks because of the low temperatures used), and the lattice parameter systematically increased with increasing alumina from 0.509 nm for pure ZrO_2 to 0.513 nm for the 40% alumina material. When calcined at temperatures above 1000 °C, the final product was observed to crystallize in the tetragonal form. Subsequent consolidation of the powders by hot isostatic pressing at temperatures in the range 1000–1150 °C resulted in transformation to the tetragonal phase, some of which transformed back to monoclinic zirconia (m-ZrO_2) on cooling to room temperature. Strengths of up to 700 MPa were observed for these materials, with values of fracture toughness of up to 23 MPa m$^{1/2}$. It is believed that these high values arise because of the very small grain size of the starting powders when prepared via a chemical route. Clearly these results are impressive and indicate that further studies should be carried out in this system. The present paper builds on this work, using an aqueous co-precipitation route for the formation of the starting powders instead of the alkoxide route used by Inamura *et al.* [4].

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2. Experimental procedure

Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), aluminium chloride ($AlCl_3 \cdot 6H_2O$) and ammonia were used as the three starting materials for preparing 20 mol% Al_2O_3–80 mol% ZrO_2 powders. The first two were mixed in the appropriate concentrations and dissolved in distilled water to give an overall 20 : 80 alumina : zirconia molecular ratio. The solution was thoroughly stirred at room temperature, and then ammonia was quickly added to the mixed solution, with vigorous stirring until complete co-precipitation occurred. The resulting Al_2O_3–ZrO_2 gel was washed with distilled water until chloride ion free (as tested by $AgNO_3$ solution), treated ultrasonically for 45 min and then dried at 100 °C. After grinding to pass through a 200 mesh sieve, the gel powder was calcined at 450, 550 and 650 °C and at 50 °C intervals up to 1300 °C, each for 2 h, followed by sieving again through 100 mesh to give the final Al_2O_3–ZrO_2 powder. Pure zirconia and alumina powders were also prepared by the same route.

Phase identification of the Al_2O_3–ZrO_2 powder as well as the pure zirconia and pure alumina powders calcined at different temperatures was carried out by X-ray diffraction (XRD) using a Hägg–Guinier focusing camera with Cu $K\alpha_1$ radiation. Phase composition analysis of the Al_2O_3–Al_2O_3 powders calcined at 800–1300 °C was carried out by special software attached to a Rigaku RINT2500VHF system.

Differential thermal analysis (DTA) was conducted in an argon gas atmosphere (50 ml min^{-1}) at a heating rate of 5 °C min^{-1}. Pure α-Al_2O_3 was used as the reference standard.

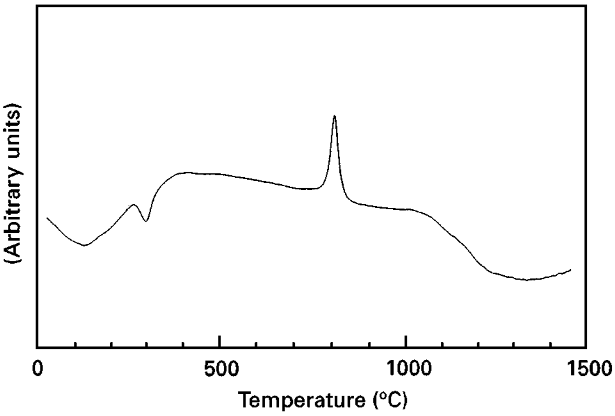

Figure 1 DTA curve for 20 mol% Al_2O_3–80 mol% ZrO_2 calcined at 450 °C.

TABLE I Phase identification of pure Al_2O_3 and pure ZrO_2 powders calcined at different temperatures

Calcination temperature (°C)	Pure Al_2O_3	Pure ZrO_2
500	γ	m
600	γ	m
700	γ	m
800	γ	m
900	θ	m
1000	θ	m
1050	θ	m
1100	$\theta + \alpha$	m
1200	α	m
1400	α	m
1530	α	m

3. Results

After co-precipitation and calcination of the 20 mol% Al_2O_3–80 mol% ZrO_2 composition, no crystalline phases were observed when the sample was calcined at temperatures below 780 °C. The DTA curve for the sample after calcination at 450 °C (Fig. 1) shows a broad endothermic peak at 150 °C followed by a sharp endothermic peak at 310 °C. These peaks are believed to correspond to the desorption of adsorbed water, the latter in the form of OH groups. The exothermic peak observed at 790 °C corresponds to the crystallization of the sample, and this temperature is in satisfactory agreement with the temperature of 780 °C observed for the appearance of crystalline peaks on XRD photographs. Table I shows the results of calcining the pure alumina and pure zirconia precipitated gels at increasing temperatures. In the case of the zirconia gel, crystallization started at 450 °C with the formation of m-ZrO_2. This is the stable form of zirconia under these conditions and crystallizes directly rather than forming by transformation from the tetragonal form as observed in samples cooled from higher temperatures. The alumina sample again showed dehydration above 400 °C, with the formation of crystalline γ-Al_2O_3. With increasing temperature, this transformed to the θ form above 900 °C, and then the final stable α form was observed in samples calcined at temperatures above 1200 °C. These results are consistent with dehydration of hydrated alumina samples not prepared via the gel route [5].

The crystalline phases formed as a result of calcining the 20 mol% Al_2O_3–80 mol% ZrO_2 sample above 780 °C are listed in Table II. The initially formed cubic phase remains stable to 900 °C, and then at higher temperatures it transforms into a tetragonal phase, this transformation being virtually complete just above 1000 °C. As the t-ZrO_2 phase appears, so do trace amounts of θ-Al_2O_3, showing that the alumina is present in the t-ZrO_2 and c-ZrO_2 phases at lower temperatures, but this solubility has now been exceeded. Above 1100 °C there is a sudden change in the phase assemblage. m-ZrO_2 now becomes the major phase in the products and, with increasing temperature, the amount of m-ZrO_2 increases at the expense of the tetragonal phase, up to the highest temperatures investigated. Meanwhile the residual alumina content increases up to 1150 °C but then, above this temperature, remains approximately constant, transforming to the stable α form above 1200 °C.

Table III shows unit-cell dimensions measured for the c-ZrO_2 and t-ZrO_2 phases after calcining at increasing temperature. It can be seen that there is a slight increase in the unit-cell dimensions of both phases with increasing temperature.

TABLE II Phase compositions of 20 mol% Al_2O_3–80 mol% ZrO_2 powders calcined at different temperatures

Calcination temperature (°C)	c-ZrO_2 (mol%)	t-ZrO_2 (mol%)	m-ZrO_2 (mol%)	θ-Al_2O_3 (mol%)	α-Al_2O_3 (mol%)
800	100	–	–	–	–
900	99	1	–	–	–
950	98	2	–	–	–
1000	29	70	–	1	–
1050	–	97	–	3	–
1100	–	23	72	5	–
1150	–	17	75	8	–
1200	–	10	82	4	4
1250	–	6	88	1	5
1300	–	4	91	–	5

TABLE III Unit-cell dimensions of c- and t-ZrO_2 phases after calcination

Calcination temperature (°C)	c-ZrO_2		t-ZrO_2		
	a (nm)	*V* (nm^3)	*a* (nm)	*c* (nm)	*V* (nm^3)
800	0.507 23	0.1305	0.505 72	0.514 30	0.1315
900	0.508 23	0.1313	0.506 84	0.517 35	0.1329
950	0.508 30	0.1313	0.507 09	0.515 50	0.1326
1000	–	–	0.507 97	0.518 82	0.1339
1100	–	–	0.508 55	0.519 20	0.1343

4. Discussion

Whereas it has previously been accepted that there is a negligible solubility of alumina in the zirconia fluorite lattice, the present results show that this is certainly not the case when atomically mixed Zr–Al–O powders are used as the starting materials.

The co-precipitation route is one of many chemically based procedures which give mixing on the atomic level. After the bulk of the water is removed at 100 °C, both zirconium and aluminium remain coordinated by O and OH groups, but the high viscosity of the suspension prior to dehydration indicates that polymerization has occurred within the final structure to give large structural units consisting of mixed Zr and Al cations linked by O and OH groups. DTA data (Fig. 1) show that the bulk of the remaining OH content comes off in the form of water at about 300 °C but, at higher calcination temperatures, some OH still remains, which is only finally removed above about 1150 °C. After calcination, the powder can be envisaged as a cross-linked mix of Zr–O, Zr–OH, Al–O and Al–OH bonds. The X-ray data listed in Table II show that, after calcination at 800 °C, the powder has a certain crystalline structure, even though the broadened lines indicate a small particle size for the crystalline regions (4.4 nm after calcination at 800 °C; 31 nm after calcination at 1050 °C), consistent with previously reported grain sizes of 50 nm after hot isostatic pressing at 1000–1150 °C [4]. The face-centred cubic (f.c.c.) pattern indexes on a fluorite lattice very similar to that of c-ZrO_2 itself, but with a slightly decreased lattice parameter (see Table III). No unindexed lines remain, showing that aluminium must be present either in the fluorite zirconia lattice or in as yet uncrystallized material in between the zirconia grains. When these data are compared with those of pure ZrO_2 and pure Al_2O_3 materials prepared by the same chemical route (Table I), the results are completely different. Thus ZrO_2 crystallizes in the monoclinic form at all temperatures above 450 °C and Al_2O_3 crystallizes first as γ between 500 and 850 °C, with subsequent transformation to θ, and finally to α as the temperature is increased to 1200 °C. Both sets of results are entirely consistent with the expected forms of zirconia and alumina stable under these conditions. The contrast with the present results for ZrO_2–Al_2O_3 co-precipitated powders presents strong evidence that aluminium is dissolved in the zirconia lattice in these samples.

It would be expected that the simultaneous presence of Zr and Al in the final calcined powders would hinder crystallization as compared with either of the two pure powders alone. The facts that there are no zirconium aluminates and that neither zirconia nor alumina forms a solid solution in the other show that the two lattices are not geometrically compatible. However, at the lower temperatures used here, and also possibly because of the presence of residual OH groups, the fluorite lattice is able to form from the originally amorphous gel. Thus, for example, a Zr–O bond can be replaced in zirconia by Al–OH without valency imbalance. Moreover, whereas the Zr–O bond (0.22 nm) in c-ZrO_2 is considerably longer than the Al–O bond in α-Al_2O_3 (about 0.192 nm), the Al–OH bond in gibbsite ($Al(OH)_3$) or boehmite or diaspore (AlOOH) is about 0.2 nm which is increasing towards the zirconia value. Moreover, hydrogen bonding within the oxygen lattice may also assist in the formation of an apparently uniform fluorite lattice, when neither Zr^{4+} nor Al^{3+} at these temperatures is stable in an environment of eight oxygen atoms. A further reason for the appearance of an ordered fluorite lattice from the disordered Zr–Al–O–OH arrangement in the as-precipitated gel may relate to thermodynamic considerations. The observation (Table I) that m-ZrO_2 will crystallize at the temperatures above 450 °C shows that thermodynamically zirconia can easily crystallize at the temperatures used here for the mixed powders. The free energy of a crystallized Zr–Al–O fluorite lattice can become more negative than alternative arrangements if the entropy increase associated with Zr–Al ordering outweighs the reduced lattice energy of the partially ordered final arrangement; alternatively, the crystalline Zr–Al–O phase may be metastable, forming solely for kinetic reasons. Thus, for a well-mixed distribution of Zr and Al atoms, diffusion distances needed to achieve a regular distribution of atoms will be small, and f.c.c. metal ordering schemes (e.g., of the Cu_3Au type) are well known and would easily provide the basis for the metal atom distribution observed here.

The results obtained for calcining the mixed Al_2O_3–ZrO_2 powders at higher temperatures (Table II) show that the cubic phase becomes unstable above 950 °C in preference to the tetragonal form, with some Al coming out of the lattice. It is believed that the driving force for this transformation is the further loss of OH from the cubic lattice, and since 2 (OH) are required to produce 1 mol of H_2O, the resulting loss of oxygen from the lattice automatically necessitates a reorganization. At these higher temperatures, diffusion of Zr and Al within the oxygen framework becomes possible, and it is more stable for local regions of alumina to emerge, leaving a more Zr-rich t-ZrO_2 lattice behind. The relatively small (less than 3 mol%) levels of θ-Al_2O_3 observed suggest that alumina is still present in the t-ZrO_2 lattice because, at these temperatures (1050 °C), Al would not stably remain in an amorphous form. The data show that the transformation from c-ZrO_2 to t-ZrO_2 + θ-Al_2O_3 takes place over a narrow temperature range, indicating that kinetic restraints are not hindering movement towards increased thermodynamic stability, and that diffusion within powder grains to give local Al-rich clusters can proceed easily at these temperatures.

It is interesting that the t-ZrO_2 phase formed under these conditions does not transform to the monoclinic form on cooling, unlike equivalent pure zirconia powders. This is further evidence that Al is present in the t-ZrO_2 lattice. The small grain size of these powders is not believed to exercise any stabilizing influence on the t-ZrO_2 phase, because the work on pure zirconia powders gave similar grain sizes but in this case transformation to m-ZrO_2 did occur.

Further increase in heat-treatment temperature results in an immediate decrease in the amount of t-ZrO_2, with a corresponding increase in the amount of m-ZrO_2 formed. At the same time, more θ-Al_2O_3 appears. This is further evidence that the t-ZrO_2 phase contains Al in the lattice, and this is now being expelled to leave essentially pure zirconia, which on cooling transforms to m-ZrO_2 as expected. The rate of this reaction appears to be slower than the previous c → t transformation, possibly for diffusional reasons. Finally, above 1150 °C, θ-Al_2O_3 is no longer stable and, with loss of the trace amounts of residual OH, transforms to the final α-Al_2O_3, in contrast with the f.c.c. oxygen arrangement in all other Al-containing phases observed in this study and may provide a reason why removal of final traces of t-ZrO_2 is not complete even up to the highest heat-treatment temperatures used in the present study (1300 °C). Diffusion of aluminium from central regions of grains to the outside may be responsible for this low rate of transformation.

The change in unit-cell dimensions of the cubic and tetragonal phases with increasing temperature shown in Table III support the above arguments. All cell dimensions increase, heading towards the values for pure c-ZrO_2 and t-ZrO_2 (unit-cell volumes, 0.1319 nm^3 and 0.1377 nm^3, respectively), consistent with the removal of alumina from the lattice. The apparent decrease in the c parameter of the 950 °C t-ZrO_2 phase is probably due to a high error arising from the very small amount of t-ZrO_2 in this sample (see Table II).

The sequence of phases observed during heat treatment of these powders provides an interesting contrast with the normal order of phase stability in zirconia materials which proceeds in the order m → t → c with increasing temperature. This provides further evidence for the presence of Al (and possibly also of OH) in the fluorite lattice, the stabilizing effects of which interfere with the normal order of phase stability.

A surprising feature of the present results is that the cell dimensions observed for the c- and t-ZrO_2 phases are very little different from accepted literature values for pure c- and t-ZrO_2. The above discussion has argued that all the original 20 mol% Al_2O_3 is present in the c-ZrO_2 phase observed and that perhaps in excess of 10 mol% Al_2O_3 is present in the t-ZrO_2 phase. Since the Al–O bond is substantially smaller than the Zr–O bond, some reduction in lattice parameter would have been expected for the c- and t-ZrO_2 phases. Despite the increased line breadths of XRD lines which make it difficult to obtain accurate unit-cell parameters, any decrease in lattice parameter is not larger than the standard deviation. The most likely explanation which can be offered at this stage is that the OH present in the lattice also contributes to an increase in lattice parameter because of the larger value for the Al–OH bond (0.2 nm) compared with the Al–O value (0.192 nm).

5. Conclusions

As established by Inamura *et al.* [4], alumina dissolves in the fluorite lattice of zirconia at low (below 1000 °C) temperatures, when oxides of the elements are sintered together in the form of intimately mixed powders, such as when prepared via either sol–gel or co-precipitation routes. The present work, based on mixing zirconium oxychloride and aluminium chloride powders, gives identical results with those obtained in previous work [4] based on mixed alkoxides.

Incorporation of aluminium into the fluoride lattice is confirmed by the observation of a c-ZrO_2 phase in the temperature range 800–950 °C, with a reduced lattice parameter compared with pure c-ZrO_2. With increasing temperature, this cubic phase becomes unstable, decomposing into a t-ZrO_2 phase with reduced Al content, the balance of alumina appearing in the form of θ-Al_2O_3. With increasing temperature, this t-ZrO_2 phase also loses alumina and in so doing becomes destabilized, transforming into m-ZrO_2 on cooling.

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