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Phase transformation of yttria-stabilized zirconia plasma-sprayed coatings in a humid atmosphere

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The tetragonal to monoclinic phase transformation resulting from the hydrothermal ageing of 4–20 mass % yttria-stabilized zirconia plasma-sprayed coatings formed from commercial powders has been studied with respect to the Y_2O_3 distribution inside each coating. The phase transformation was prevented when the nominal Y_2O_3 concentration was greater than 8 mass % with its point to point distribution ranging between 6.82 to 9.90 mass %. It is suggested that a close correlation exists between the durability of the tetragonal phase in a humid atmosphere and the Y_2O_3 distribution in the tetragonal zirconia coatings. A content of 6.3–6.8 mass % Y_2O_3 was calculated to be necessary to prevent the transformation.

1. Introduction

It is known that polycrystalline yttria-stabilized tetragonal zirconia exhibits a high fracture strength, toughness, low heat conductivity and high thermal expansion. Therefore, zirconia ceramics are promising materials for application at high temperatures. In particular, plasma-sprayed yttria-stabilized zirconia is a candidate for application as a thermal barrier coating on gas turbine blades due to its low heat conductivity and high thermal expansion [1, 2].

However, the excellent mechanical properties of Y-TZP (yttria-stabilized tetragonal zirconia polycrystals) are degraded by low-temperature ageing in air [3]. This degradation is believed to be caused by a tetragonal to monoclinic phase transformation at the interface between the ambient atmosphere and the material. Of particular interest in this respect is the observation that the degradation rate due to the low-temperature ageing is higher in a humid atmosphere than in a dry atmosphere [4–6].

Several theories have been proposed to explain the mechanism of the phase transformation in a humid environment. Lange *et al.* [7] have suggested that the transformation is induced by a depletion of the stabilizing Y element in Y-TZP caused by a reaction with water vapour that results in the formation of $Y(OH)_3$. Sato and Shimada [8] on the other hand have suggested that the phase transformation is caused by a chemical reaction between t-ZrO_2 and H_2O.

It has been shown that the higher the stabilizing element concentration in the tetragonal zirconia the lower is the monoclinic ZrO_2 fraction formed [4, 6–15], and that this monoclinic fraction finally saturates during the ageing in humid air leaving an unreacted tetragonal phase content [4, 6, 9–11, 13, 14]. Furthermore, Yashima *et al.* [6] and Schubert and Petzow [15] have suggested that the distribution of the stabilizing element can affect the monoclinic phase fraction after hydrothermal ageing.

However, the relationship between the stabilizing element distribution and the phase transformation behaviour in humid air has not been fully clarified nor has the reason why the monoclinic fraction finally saturates been satisfactorily explained. In addition the phase transformation that occurs on the low-temperature ageing of plasma sprayed coatings has not been investigated.

The present study deals with the tetragonal to monoclinic phase transformation in yttria-stabilized zirconia plasma-sprayed coatings during hydrothermal ageing. In particular, attention was focused onto the relationship between the Y_2O_3 distribution and the extent of the monoclinic fraction formed. The critical Y_2O_3 concentration to inhibit the phase transformation was determined.

2. Experimental procedure

The Y_2O_3 stabilized zirconia powders used in this work were obtained from a commercial source. The nominal powder compositions are listed in Table I. The grain size distributions for all the powders ranged between 44–88 μm. The 4YZ, 6YZ, 8YZB and 20YZ powders are fused and crushed powders and the 8YZA powder is an agglomerated and sintered powder. Each test piece was composed of a substrate (SUS304, 70 × 50 × 3 mm), a metal (NiCoCrAlY; Ni–23.8Co–16.7Cr–13.0Al–0.65Y; mass %) bonding layer (150 μm) and the Y_2O_3 stabilized zirconia layer (250 μm thick). The two layers were prepared by the atmospheric plasma-spray (APS) method using the conditions listed in Table II.

TABLE I Compositions of the zirconia powders used in this study

Powder	Y_2O_3 concentration (mass %)	Grain size (μm)	Manufacturing method
4YZ	4	44–88	FC
6YZ	6	44–88	FC
8YZA	8	44–88	AG
8YZB	8	44–88	FC
20YZ	20	44–88	FC

FC: fused and crushed. AG: agglomerated and sintered.

TABLE II Plasma spraying parameters

Parameter		Value
Arc current		900 A
Arc voltage		37 V
Gas pressure	Ar	0.34 MPa
	He	0.34 MPa
Spray distance		$8–11 \times 10^{-2}$ m

TABLE III Chemical analysis results of plasma-sprayed powders and coatings

Specimens		Y_2O_3 (mass %)	Al_2O_3 (mass %)	Fe_2O_3 (mass %)	SiO_2 (mass %)
Powders	4YZ	4.37	0.14	0.15	0.11
	6YZ	6.47	0.15	0.05	0.11
	8YZA	7.74	1.29	0.08	0.30
	8YZB	7.73	1.11	0.06	0.18
	20YZ	19.9	0.18	0.05	0.11
Coatings	4YZ	4.33	0.19	0.13	0.06
	6YZ	6.42	0.19	0.05	0.07
	8YZA	8.38	0.21	0.04	0.04
	8YZB	8.20	1.40	0.09	0.32
	20YZ	20.10	0.15	0.02	0.02

The determination of the starting powder and coating compositions was performed using inductively coupled plasma (ICP) emission spectroscopy. The Y_2O_3 distribution in the 4YZ, 6YZ, 8YZA and 8YZB coatings was measured by electron probe X-ray microanalysis (EPMA) using a 3.0 mol % (5.4 mass %) $Y_2O_3–ZrO_2$ sintered body as a standard. For each specimen, 40 analysis points were selected, each point being 1 μm in diameter.

The hydrothermal ageing tests were carried out in a saturated steam atmosphere of 0.002–1.57 MPa, produced in an autoclave, in the temperature range between room temperature and 473 K for times between 0–100 h.

The phases present in the plasma-sprayed surface layer were identified by X-ray diffraction (XRD) analysis. Diffraction scans were collected over the angular (2θ) range of 27° to 33° in order to estimate the monoclinic to (tetragonal + cubic) zirconia ratio. The monoclinic fraction, X_m, is defined via the following equation [16]:

$$X_m = \frac{I(1\,1\,\bar{1})_m + I(1\,1\,1)_m}{I(1\,1\,\bar{1})_m + I(1\,1\,1)_{t,c} + I(1\,1\,1)_m}. \quad (1)$$

where, $I(1\,1\,\bar{1})_m$ is the integrated intensity of the $(1\,1\,\bar{1})$ reflection and $I(1\,1\,1)_m$ is that of the (1 1 1) reflection, both reflections belonging to the monoclinic phase, and $I(1\,1\,1)_{t,c}$ is that of the (1 1 1) reflection of the tetragonal or cubic phase.

The cross-sectional microstructures of the aged zirconia layers were observed by scanning electron microscopy (SEM).

3. Results and discussions
3.1. Phases and Y_2O_3 distribution in the plasma-sprayed zirconia coatings

Table III lists the chemical compositions of the starting powders and the yttria-stabilized zirconia plasma-sprayed coatings. The yttria content did not change significantly during the plasma-spraying process during which the starting powders were melted in the plasma arc flame and then quenched on the substrate.

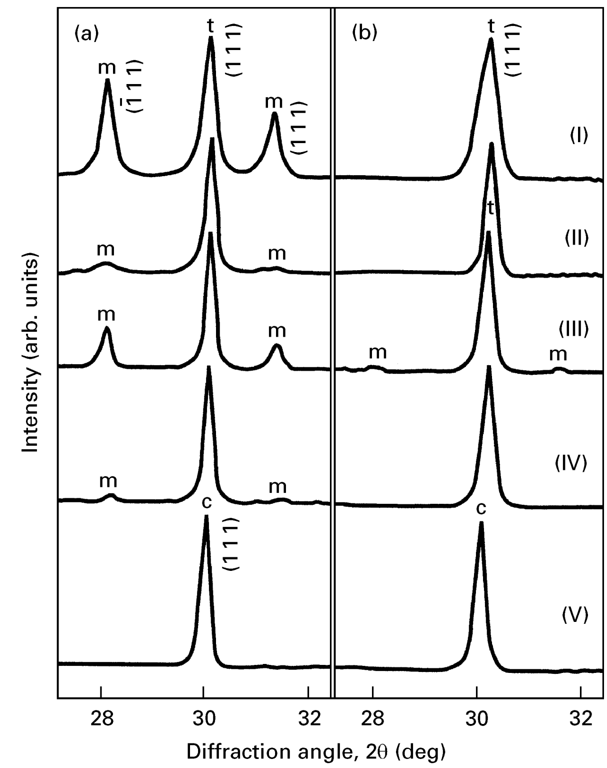

Figure 1 Typical X-ray diffraction patterns of (a) plasma-sprayed powders and (b) as-sprayed coatings. (i) 4YZ; (ii) 6YZ; (iii) 8YZA; (iv) 8YZB and (v) 20YZ.

Fig. 1(a and b) shows typical X-ray diffraction patterns of the powders and plasma-sprayed coatings. The monoclinic fractions in the specimens (X_m) are listed in Table IV. The 4YZ, 6YZ and 8YZB powders, which were fused and crushed, contained some fractions of the monoclinic phase and the X_m value decreased with the increase of yttria content. During the plasma spraying process, the monoclinic phase fraction decreases significantly and the 4YZ, 6YZ and 8YZB coatings are purely tetragonal. However, the 8YZA coating still contained a small amount of the monoclinic phase. Both the 20YZ powder and plasma-sprayed coating solely consisted of the cubic phase.

We believe that the monoclinic phase fraction in the 4YZ, 6YZ, 8YZA and 8YZB coatings decreased during the plasma spraying process because of yttrium diffusion produced by re-melting of the plasma-sprayed powders.

Fig. 2(a–d) shows the EPMA-determined Y_2O_3 distributions in the 4YZ, 6YZ, 8YZA and 8YZB coatings. The Y_2O_3 content of the 4YZ, 6YZ and 8YZB coatings ranged from 2.39 to 5.81, from 5.27 to 7.50, and from 6.82 to 9.90 mass %, respectively. These ranges of Y_2O_3 distribution overlap each other and their standard deviations were 0.56, 0.53 and 0.61 mass %. On the other hand, the Y_2O_3 content of the 8YZA coating exhibited considerable scatter with measured values of 1.33 to 14.82 mass % with a standard deviation of 2.50 mass %.

TABLE IV Monoclinic phase fraction, X_m, of plasma-sprayed powders and plasma-sprayed coatings

	X_m (mol %)	
Composition	Powders (as-received)	Coatings (as-sprayed)
4YZ	55.80	0.00
6YZ	11.84	0.00
8YZA	30.95	4.57
8YZB	1.30	0.00
20YZ	0.00	0.00

As shown in Fig. 2(a–d), the Y_2O_3 distribution in the 4YZ, 6YZ and 8YZB coatings were relatively uniform. Whilst the scatter in the Y_2O_3 content values in the 8YZA coating implies tetragonal zirconia regions with much lower Y_2O_3 concentrations than average. Furthermore, the Y_2O_3 distribution in the 8YZA sample was more nonuniform compared with those of the 4YZ, 6YZ and 8YZB samples and spread to a lower value than those of the 4YZ and 6YZ samples.

The EPMA analyses show the uniformity of the Y_2O_3 distribution in each plasma-sprayed coating, which is also demonstrated in the XRD patterns. As shown in Fig. 1, only in the case of the 8YZA plasma-sprayed coating could any monoclinic phase be observed. Generally, Y_2O_3 solubility in the monoclinic phase of zirconia-yttria polycrystals is low [17]. From these results, it is suggested that the monoclinic phase present in the 8YZA coating reflects the existence of a low Y_2O_3 composition region in the coatings. On the other hand, in the plasma spray coatings that had no detectable monoclinic phase, namely 4YZ, 6YZ, 8YZB and 20YZ, the Y_2O_3 distributions do not include this low concentration region. In the high-Y_2O_3-content zirconia coatings such as 6YZ, 8YZB and 20YZ, in particular, no area in which the Y_2O_3 concentration is lower than 5 mass % exists.

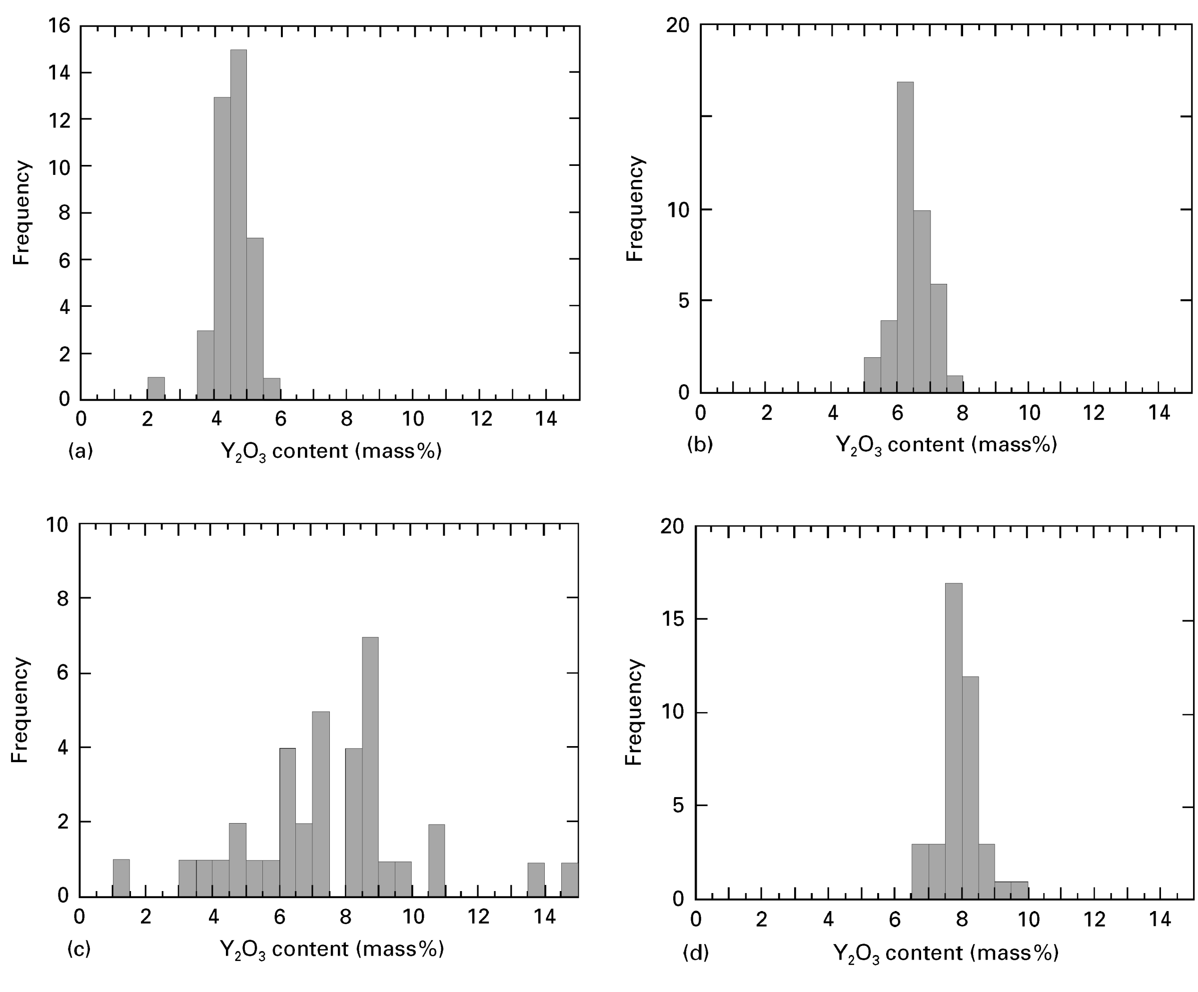

Figure 2 Distribution of Y_2O_3 concentration in plasma-sprayed zirconia coatings measured by EPMA; (a) 4YZ, (b) 6YZ, (c) 8YZA, (d) 8YZB.

3.2. Phase change during ageing in a humid atmosphere

Fig. 3 shows the temperature dependence of the monoclinic phase fraction, X_m, of the studied coatings after ageing in a saturated steam atmosphere (0.002–1.57 MPa), at temperatures from 343 to 473 K for 50 h. The t → m phase transformation occurred in the 4YZ, 6YZ and 8YZA coatings. However no phase transformation was observed in the 8YZB and 20YZ coatings.

These results indicate that the phase transformation can occur only in coating consisting purely or predominantly of tetragonal zirconia, namely 4YZ, 6YZ and 8YZA, but not in the 20YZ coating that was a single phase cubic material. It is particularly noteworthy that the phase transformation occurred in the 8YZA coating, but not in the 8YZB coating even though both of these coatings had the same Y_2O_3 content.

In the 4YZ, 6YZ and 8YZA coatings, a greater monoclinic phase content was observed with increasing ageing temperature and steam pressure to which the coatings were exposed. The fraction of the monoclinic phase after ageing increased with a decrease in the Y_2O_3 composition.

Fig. 4 shows the ageing time dependence of the monoclinic phase fraction after an hydrothermal ageing test, at 473 K for 0–100 h in a steam pressure of 1.57 MPa. The X_m value for each sample quickly saturated (within 10 h) and then showed no change even after ageing for 100 h. This relationship between the Y_2O_3 concentration and the fraction of monoclinic phase after ageing obtained for the plasma-sprayed coatings is in line with the results for sintered bodies [6, 8–11, 13].

Fig. 5(a and b) shows X-ray diffraction patterns of the plasma-sprayed zirconia coatings before and after the hydrothermal ageing tests. It is clear that the tetragonal phase remained in the plasma-sprayed coatings even after the ageing tests.

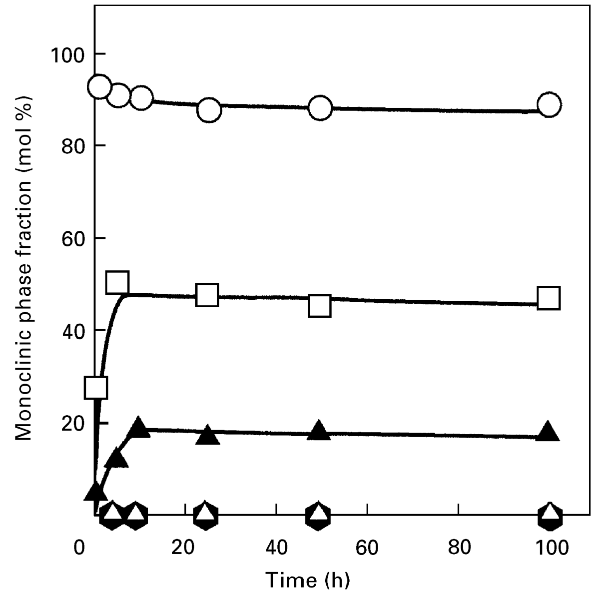

Figure 4 Monoclinic phase fraction in the plasma-sprayed zirconia coatings; (○) 4YZ; (□) 6YZ; (▲) 8YZA; (△) 8YZB and (⬢) 20YZ at 473 K in a saturated steam atmosphere.

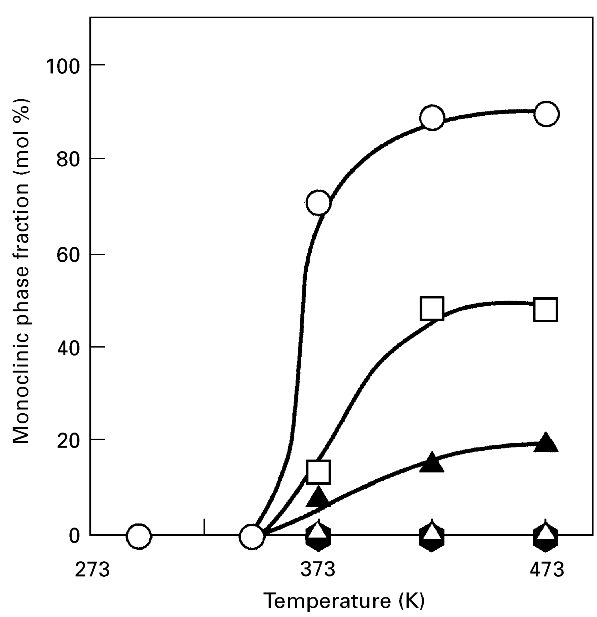

Figure 3 Monoclinic phase fraction in the plasma-sprayed zirconia coatings; (○) 4YZ; (□) 6YZ; (▲) 8YZA; (△) 8YZB and (⬢) 20YZ after ageing in a saturated steam atmosphere at various temperatures.

By summarizing the results shown in Figs 2–5(a and b) it is shown that both cubic and tetragonal zirconia phases are observed after the ageing tests of the plasma-sprayed coatings. Furthermore, it was found that the 8YZB coating that contained tetragonal zirconia with a relatively uniformly distributed 8 mass % Y_2O_3, had not transformed into the monoclinic phase even after ageing for 100 h at 473 K in a steam pressure of 1.57 MPa. In addition tetragonal zirconia that had enough Y_2O_3 at every part of the layer did not transform to the monoclinic phase during ageing in a humid atmosphere. These results further suggest that the tetragonal zirconia compositions, which did not transform to the monoclinic phase during the hydrothermal ageing have more Y_2O_3 than a critical concentration that prevents the phase transformation [11, 18].

In order to estimate the critical Y_2O_3 concentration that suppress the tetragonal to monoclinic phase transformation during hydrothermal ageing, at 473 K in a steam pressure of 1.57 MPa, the relationship between the Y_2O_3 distribution and the monoclinic phase content after ageing was investigated.

3.3. Relationship between the Y_2O_3 distribution and phase transformation during ageing

We observed that in the 8YZB plasma-sprayed coating, which had a relatively uniform Y_2O_3 distribution, the tetragonal to monoclinic phase transformation during hydrothermal ageing was suppressed while in the 8YZA sample which had regions having less than 5 mass % Y_2O_3, the phase transformation occurred. Furthermore, out of the plasma-sprayed coatings which had a relatively uniform Y_2O_3 distribution,

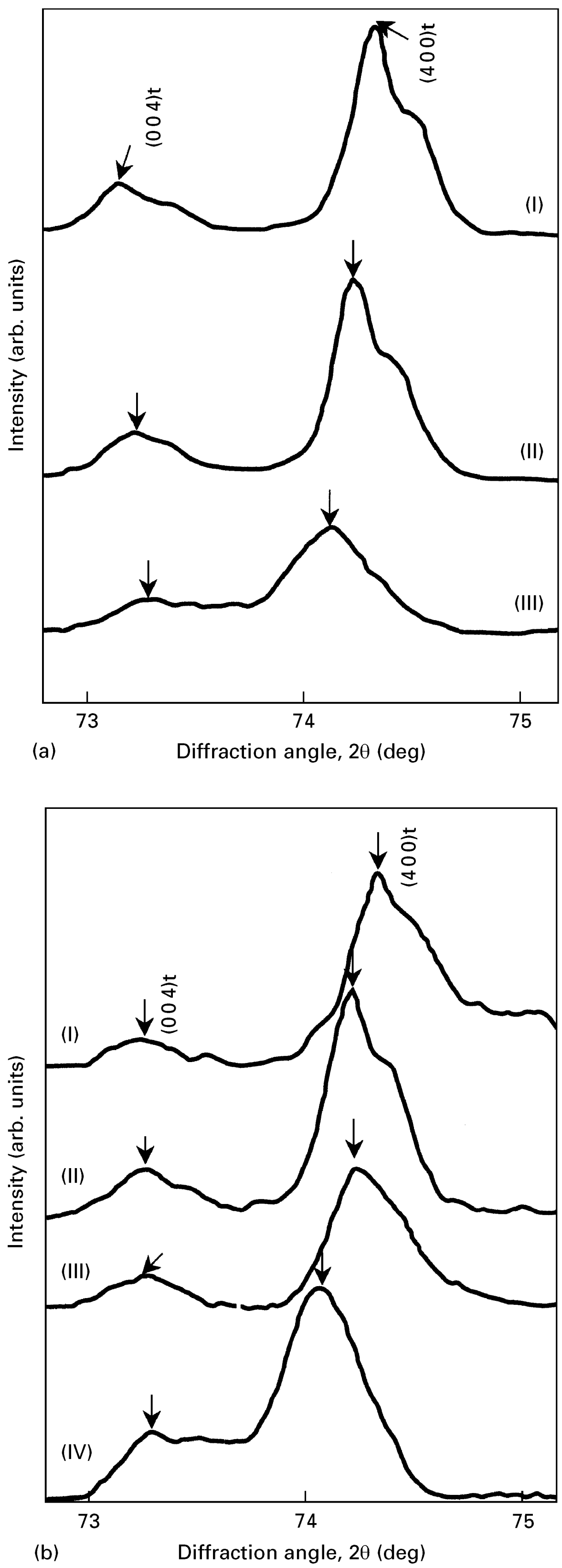

Figure 5 X-ray diffraction patterns of the surface of plasma-sprayed zirconia coatings; (a) before the ageing test, (i) 4YZ, (ii) 6YZ and (iii) 8YZA; (b) after the ageing test in a saturated steam atmosphere. (i) 4YZ, 373 K for 50 h; (ii) 6YZ, 373 K for 50 h; (iii) 6YZ, 473 K for 50 h and (iv) 8YZA, 473 K for 50 h.

namely the 4YZ, 6YZ and 8YZB coatings, the phase transformation was suppressed only in the case of the 8YZB coating.

From these results, we infer that the 8YZB plasma-sprayed coating is composed of tetragonal zirconia that had a sufficient Y_2O_3 concentration at every part of the layer to prevent the tetragonal to monoclinic phase transformation during the hydrothermal ageing. As a result, the phase transformation did not occur in this coating.

From this point of view, it is suggested that the monoclinic phase fraction saturates within a short time as shown in Fig. 4 because there are tetragonal zirconia regions in which the Y_2O_3 concentration exceeds a critical value even in the 4YZ, 6YZ and 8YZA coatings.

We attempt to estimate the critical Y_2O_3 concentration at 473 K assuming that the Y_2O_3 distribution in the zirconia coatings can be approximated by a Gaussian distribution. Let x, M and σ be the Y_2O_3 concentration, its mean value and the standard deviation, respectively. Then the probability density function, $f(x)$, can be written as:

$$f(x) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left\{-\frac{(x-M)^2}{2\sigma^2}\right\} \quad (2)$$

The critical Y_2O_3 concentration that suppresses the tetragonal to monoclinic phase transformation during hydrothermal ageing at 473 K in a steam pressure of 1.57 MPa, X_c, was calculated by:

$$X_m = \int_{-\infty}^{X_c} f(x)\,dx \quad (3)$$

Table V shows the calculated critical Y_2O_3 concentrations. The critical Y_2O_3 concentration ranges from 6.27 to 6.82 mass % except for the case of the 4YZ coatings. These values are almost equal considering the EPMA experimental error of 1 mass %. In the case of the 4YZ coating, the X_m value is large (see Fig. 4). For this reason, small changes of σ result in large uncertainties in estimating the critical Y_2O_3 concentration.

From these results, we conclude that the critical Y_2O_3 concentration for the transformation of the tetragonal phase to monoclinic phase in the plasma-sprayed zirconia coatings is 6.3–6.8 mass % at 473 K.

It has been suggested that the phase stability of tetragonal zirconia is influenced by the grain size and strain in addition to the Y_2O_3 content [8–15, 18, 19]. In order to further clarify the critical Y_2O_3 concentration, it is necessary to investigate the influence of these factors in detail.

TABLE V Critical Y_2O_3 concentration for the transformation to the monoclinic phase at 473 K

Sample	Mean Y_2O_3 concentration (mass %)	Standard deviation σ	Critical Y_2O_3 concentration (mass %)
4YZ[a]	4.33	0.56	5.02
6YZ[a]	6.42	0.53	6.39
8YZA[a]	8.38	2.50	6.27
8YZB[b]	8.20	0.61	< 6.82

[a] Calculated from a Gaussian distribution for the Y_2O_3 in the plasma-sprayed zirconia coatings measured by EPMA analysis.
[b] Estimated by the minimum Y_2O_3 concentration measured by EPMA analysis.

3.4. Microstructural changes that accompany the tetragonal to monoclinic phase transformation

Fig. 6 shows the microstructure of a cross-section of the as-sprayed zirconia coating (4YZ) obtained by SEM. Lamellar structures are observed. The microstructures of the 4YZ and 6YZ coatings after ageing are shown in Fig. 7(a and b).

The cross-sections of the plasma-sprayed coatings before ageing are smooth and flat. In each cross-section of the coatings after ageing, on the other hand, scratch-like columns (shown by circles) are observed.

Figs 6 and 7(a and b) indicate that the microstructure of the zirconia coatings after ageing are markedly different from those before ageing. This change in the microstructures of the plasma-sprayed coatings is considered to be caused by the phase transformation during the hydrothermal ageing.

Fig. 8 shows a cross-section of a typical fracture surface of the 4YZ plasma-sprayed coating. Comparing Fig. 7(a and b) with Fig. 8, the texture of the plasma-sprayed coatings after ageing looks like the fracture surface of a plasma-sprayed coating. This result indicates that the structural change caused by the tetragonal to monoclinic transformation is accompanied by a volume expansion. Thus, it is plausible that the tetragonal to monoclinic phase transformation in the zirconia coatings degrades the mechanical strength of the plasma-sprayed coatings and lowers the material life.

4. Conclusions

The tetragonal to monoclinic phase transformation which occurs in plasma-sprayed yttria-stabilized zirconia coating layers in a humid atmosphere has been studied. In tetragonal zirconia with a uniformly distributed 8 mass % Y_2O_3 this transformation does not occur. It is proposed that a tetragonal zirconia that contains more than 6.3–6.8 mass % Y_2O_3 is stable to the transformation to the monoclinic phase in a steam saturated atmosphere at 473 K.

The tetragonal to monoclinic phase transformation is accompanied by a volume expansion which causes microstructural changes in the coatings, which in turn degrades the mechanical property and influences the material life of the zirconia coating layers.

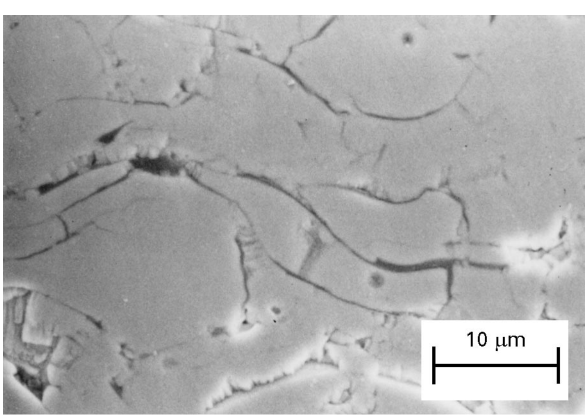

Figure 6 SEM photograph of the cross-section of an as-sprayed 4YZ coating.

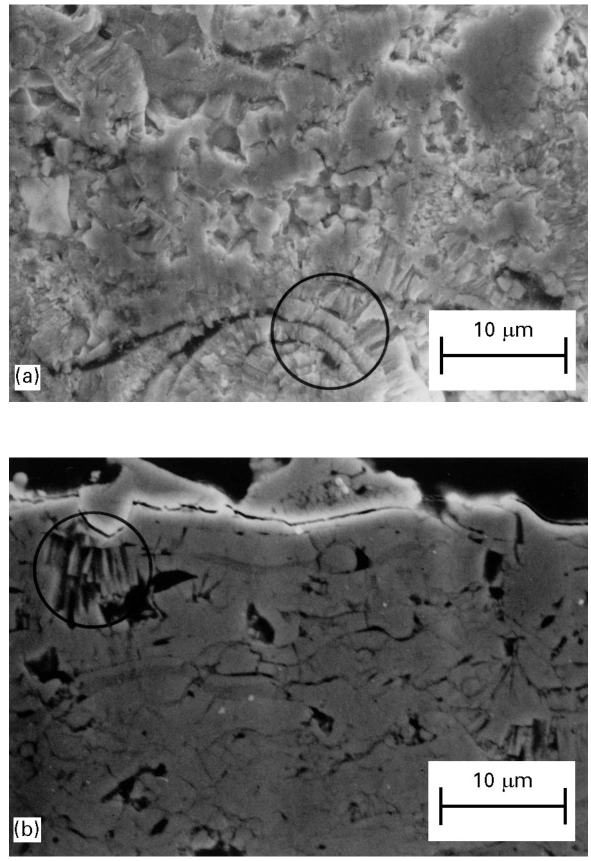

Figure 7 SEM photographs of the sample cross-section after an ageing test at 473 K, in a saturated steam atmosphere of 1.57 MPa for (a) 4YZ and (b) 6YZ coatings.

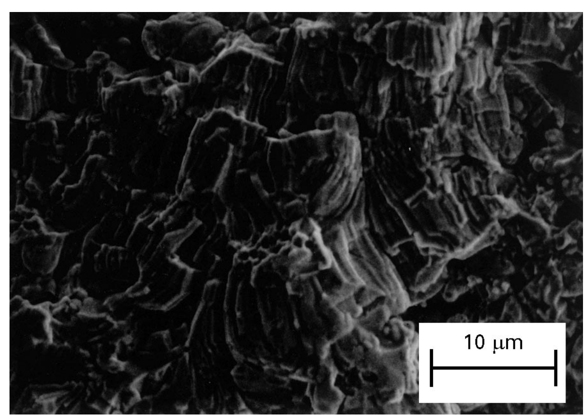

Figure 8 SEM photograph of a typical fracture surface of the as-sprayed 4YZ coating.

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