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Phase transformation during alternating aging at 473 K and at 773 K in the plasma-sprayed yttria stabilized zirconia coating

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The phase transformation of plasma-sprayed 6 mass % yttria-stabilized zirconia coatings was investigated during alternating aging under two conditions, at 473 K in saturated steam pressure and at 773 K in air. Prior to the aging, the samples were annealed at 773 K and 1073 K in order to control stress relief. Selection of the annealing temperatures caused distinct differences in the phase transformation. After the first aging at 473 K, the monoclinic phase fraction in the coatings annealed at 773 K was found to be greater than that of the coatings annealed at 1073 K. In the coatings annealed at 773 K, the decrease of the monoclinic phase fraction was observed after aging at 473 K in each cycle, while the coatings annealed at 1073 K showed an increase of monoclinic phase fraction.

1. Introduction

Zirconia ceramics have excellent mechanical properties such as high fracture strength and high fracture toughness. They also have a high thermal expansion coefficient and low thermal conductivity. Therefore, the plasma-sprayed stabilized zirconia, such as yttria-zirconia, has been developed for use as thermal barrier coatings (TBCs) for gas turbine and other engine components [1, 2].

In the zirconia ceramics, however, degradation of the mechanical properties occurs in low temperature aging because of tetragonal to monoclinic phase transformation [3–15]. Furthermore, it was reported that the Y_2O_3-concentration and distribution, zirconia grain size and stress affected the extent of the tetragonal to monoclinic phase transformation in a humid atmosphere [4–8, 11–13, 16, 17].

We studied the tetragonal to monoclinic (t → m) phase transformation during hydrothermal aging in the plasma-sprayed 4–8 mass % yttria-stabilized zirconia coatings which had been annealed at 1273 K [18]. After annealing, tetragonaility (lattice parameter ratio; c / a) of zirconia was found to be greater than that before annealing. Furthermore, after annealing at 1273 K, the monoclinic phase fraction due to the t → m phase transformation during hydrothermal aging decreased. We also found that the critical Y_2O_3 concentration for preventing this phase transformation was reduced from 6.3–6.8 mass % to less than 5.3 mass %.

The plasma-sprayed coatings are formed by the accumulation of the collision and solidification of melted powder particles. For this plasma-spray method, it was considered that residual stress may remain on the coatings. We suggested that the critical Y_2O_3 concentration for preventing this phase transformation was reduced due to stress relief by annealing.

On the other hand, the monoclinic phase which was formed after hydrothermal aging transforms to the tetragonal phase again by annealing at above 773 K in air [19]. If the tetragonal zirconia which contains less than 6 mass % Y_2O_3 were annealed at 473 K and at above 773 K repeatedly, the phase transformations, i.e., the t → m phase transformation at the 473 K and the m → t phase transformation at above 773 K would occur alternately at every annealing. The t → m phase transformation at the 473 K aging accompanies volume expansion, while the m → t phase transformation at 773 K aging results in volume shrinkage. By the expansion and shrinkage, stresses develop, and these stress seem to influence the next phase transformation. However, the detailed behavior of the phase transformations, i.e. The t → m and m → t phase transformations in the alternating aging has not been studied.

We investigated the changes of the monoclinic phase fraction of the plasma-sprayed 6 mass % yttria-stabilized zirconia coatings under alternating aging, in which hydrothermal aging treatments at 473 K in hydrothermal atmosphere and at 773 K in air. Prior to the aging, the plasma-sprayed coatings were annealed at both 773 K and 1073 K in order to control stress relief.

2. Experimental

2.1. Experimental procedure

Each test piece of the plasma-sprayed coatings was composed of a substrate (SUS304; 70 mm × 50 mm × 3 mm), a metal (NiCoCrAlY; Ni - 23.8 Co - 16.7 Cr - 13.0 Al - 0.65 Y; mass%) bonding layer and a 6 mass %

TABLE I 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

Y_2O_3 stabilized zirconia (6YZ) layer. The thickness of the metal bonding layer and zirconia layer was 150 μm and 250 μm, respectively. The two layers were prepared by the atmospheric plasma-spray (APS) method under the conditions shown in Table I. Since the monoclinic phase fraction after hydrothermal aging was influenced by the Y_2O_3 distribution, it was necessary to make the Y_2O_3 concentration within a coating uniform [17]. For this reason, the 6YZ coatings were formed from fused and crushed powders.

The average composition determination of the plasma-sprayed coatings was conducted by inductively coupled plasma (ICP) emission spectroscopy. The Y_2O_3 distribution in the 6YZ coatings was measured by electron probe microanalysis (EPMA) and transmission electron microscopy (TEM).

In order to control stress relief, annealings were performed, i.e. the samples were heated up at a rate of a 200 K/h, kept at 773 K, 1073 K and 1273 K for 1–100 h in air and then quenched in air.

The alternating aging was then carried out by repeating heating at 473 K for 50 h in a steam pressure of 1.57 MPa and at 773 K for 1 h in air. An autoclave was used for the 473 K aging test. The holding time for 473 K aging was decided so that the monoclinic phase fraction saturates sufficiently [17]. The condition of the 773 K aging was also decided in order to make the m → t phase transformation occur efficiently and to minimize an undesirable process (stress relief by this aging) during this aging.

Crystalline phases on the plasma-sprayed surface layer were identified by X-ray diffraction (XRD) analysis. Scans of 2θ between 27 and 33 degrees were conducted to estimate the monoclinic to (tetragonal + cubic) zirconia ratio. The monoclinic fraction, Xm, is defined as the following equation [20]:

$$\mathrm{Xm} = \frac{I(11\bar{1})\mathrm{m} + I(111)\mathrm{m}}{I(111)\mathrm{m} + I(111)\mathrm{t,c} + I(111)\mathrm{m}}. \quad (1)$$

where $I(11\bar{1})_\mathrm{m}$ is the integrated intensity of the $(11\bar{1})$ reflection of the monoclinic phase, $I(111)_\mathrm{m}$ is that of the (111) reflection of the monoclinic phase and $I(111)_\mathrm{t,c}$ is that of the (111) reflection of the tetragonal- or cubic phase.

Furthermore, scans of 2θ between 68 and 78 degrees were also conducted to determine the lattice parameters of the tetragonal zirconia in as-sprayed samples and samples annealed at 773 K or 1073 K, using the (400) and (004) peaks. The (400) and (331) peaks of silicon were used as internal standards. The tetragonal phase was indexed on the basis of the face-centered lattice.

TABLE II Y_2O_3 distribution and concentration in plasma-sprayed coatings measured by ICP, EPMA, and TEM-EDX

Y_2O_3 Concentration	ICP 6.4 mass %	
Y_2O_3 Distribution	EPMA	TEM-EDX
Minimum	5.27 mass %	5.42 mass %
Mean	6.77	6.72
Maximum	7.50	8.42
Standard Deviation	0.40	0.88

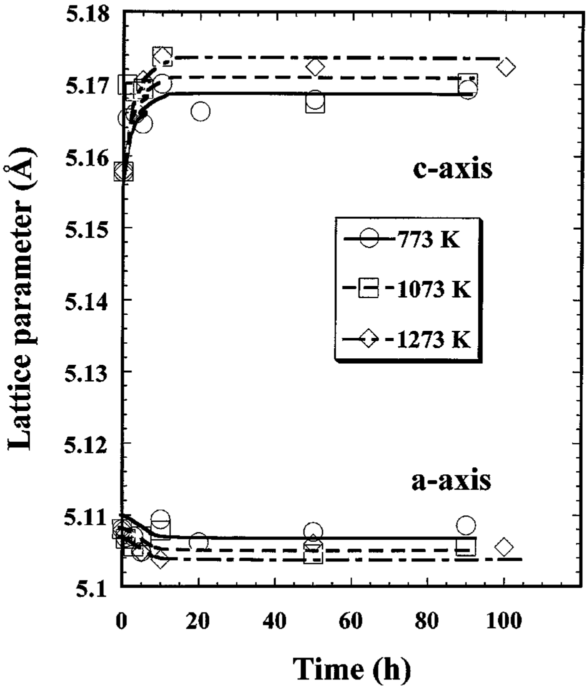

Figure 1 Lattice parameters of the 6YZ after annealing.

3. Results and discussion

3.1. Lattice parameters and tetragonality after annealing

Table II shows the Y_2O_3 concentration and distribution in the as-sprayed 6YZ coatings. The Y_2O_3 distribution was uniform and the coatings were composed exclusively of the tetragonal phase. Figs 1 and 2 show the changes of the lattice parameters and tetragonality of the 6YZ coating after annealing at both 773 K, 1073 K and 1273 K. As we reported previously, the lattice parameters of the tetragonal phase in the plasma-sprayed zirconia coatings changed by annealing in air; the a-axis shrunk, while the c-axis expanded [18]. As a consequence, tetragonality increased. After annealing at both 773 and 1073 K, the same tendency in changes of both tetragonality and the lattice parameters of the tetragonal phase was observed. The change of lattice parameters saturated after 10 h. Furthermore, the increase of tetragonality in coatings annealed at 1073 K was greater than that annealed at 773 K. However, compared with the change of tetragonality in coatings annealed at 1273 K, the tetragonality changes in coatings annealed at both 773 and 1073 K stayed smaller even after 90 h. The changes of both lattice parameters and tetragonaility were considered to be due to the residual stress relief. From the results of Figs 1 and 2, it is suggested that the

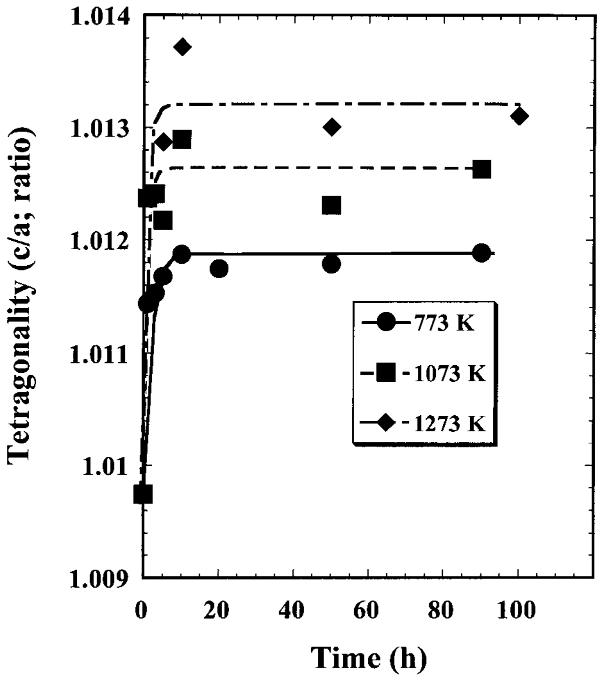

Figure 2 Tetragonality of the 6YZ after annealing.

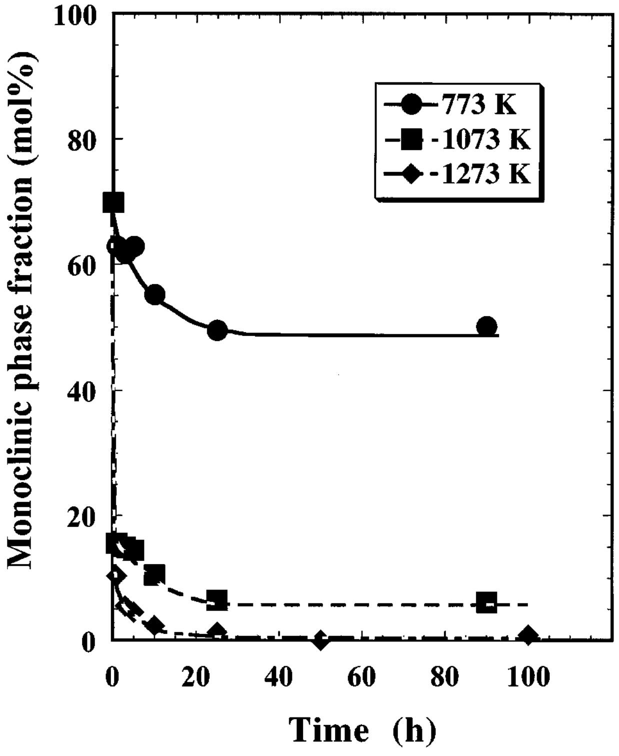

Figure 3 Monoclinic phase fraction on the coating annealed at 773 K, 1073 K, and 1273 K after hydrothermal aging at 473 K.

residual stress relief did not occur enough in samples annealed at both 773 and 1073 K.

3.2. Phase transformation of annealed samples during hydrothermal aging at 473 K

Fig. 3 shows the dependence of the monoclinic phase fraction after hydrothermal aging at 473 K on the annealing time at 773 K, 1073 K or 1273 K. The decrease of the monoclinic phase fraction with annealing time was observed. The monoclinic fraction also decreased with the increase of annealing temperature. Furthermore, the monoclinic phase fraction saturated in samples annealed for longer than 25 h and the values of monoclinic phase fraction in the samples annealed at both 773 K and 1023 K reached 50.0 and 6.1 mol %, respectively. Due to this phase transformation, all coatings annealed at 773 K was destroyed. On the other hand, in the samples annealed at 1273 K for longer than 10 h, the t → m phase transformation was not observed any more. As shown in Fig. 2, the tetragonality of samples annealed at both 773 and 1073 K did not reach that of the samples annealed at 1273 K. From these results, it is concluded that, in the plasma-sprayed coating annealed at both 773 and 1073 K, the removal of the residual stress was not sufficient. As a result, the tetragonal to monoclinic phase transformation was not prevented.

3.3. Change of monoclinic phase fraction after 473 K aging in alternating aging at 473 K and at 773 K

In the alternating aging at 473 K and at 773 K, the t → m phase transformation occurred at 473 K and the m → t phase transformation occurred at 773 K. Furthermore, all monoclinic phase which was formed by aging at 473 K was transformed back to the tetragonal phase during aging at 773 K.

Fig. 4 shows the monoclinic phase fraction after aging at 473 K in the alternating aging in the coatings annealed at 773 K for 0–25 h. In the alternating aging, some portion of the tetragonal phase transformed to the monoclinic phase during the 473 K aging. On the other hand, the monoclinic phase which was formed during the 473 K aging transformed to the tetragonal phase again by the next aging at 773 K. The monoclinic phase fraction after the aging at 773 K became

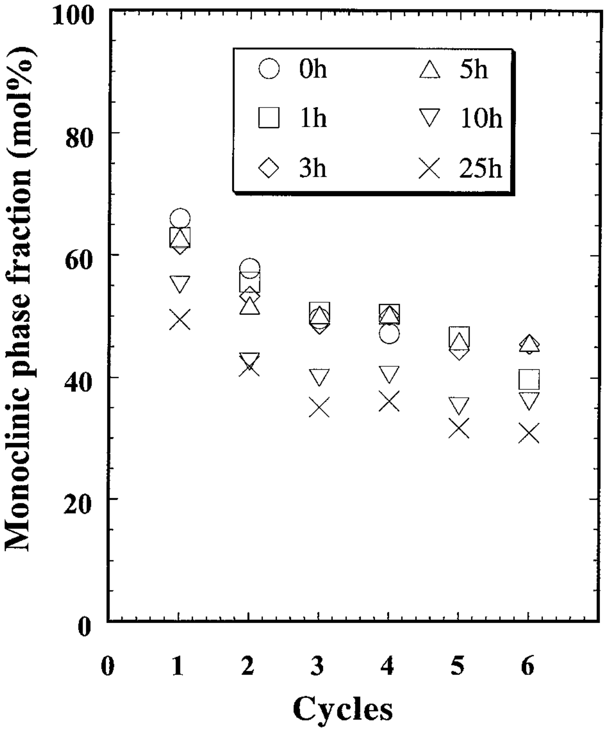

Figure 4 Monoclinic phase fraction after hydrothermal aging at 473 K in the alternating aging on the coatings annealed at 773 K for 0–25 h.

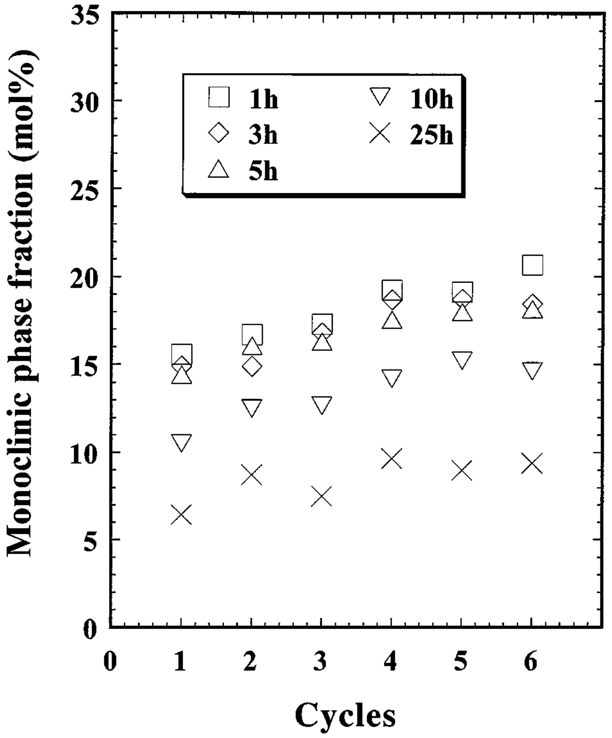

Figure 5 Monoclinic phase fraction after hydrothermal aging at 473 K in the alternating aging on the coatings annealed at 1073 K for 1–25 h.

negligible. The monoclinic phase fraction after aging at 473 K decreased gradually with the number of cycles, but saturated after 5 cycles. The most important point to note in Fig. 4 is the values of the monoclinic phase fraction after each cycle. As shown in Fig. 3, the monoclinic phase fraction did not become lower than 50 mol % even in the coatings annealed at 773 K for 90 h. In the alternating aging, however, the monoclinic phase fraction had been lower than 50 mass % after 5 cycles even in as-sprayed coatings. Furthermore, in the samples annealed at 773 K for 25 h, that value was as small as 30 mol %.

Fig. 5 shows the monoclinic phase fraction of the coatings annealed at 1073 K after aging at 473 K in the alternating aging. The monoclinic phase after aging at 473 K became richer with increasing cycles irrespective of annealing time at 1073 K. As shown in Fig. 3, the monoclinic phase fraction ranged from 6 to 16 mol % in the coatings preheated at 1073 K for 1–25 h. However, the alternating aging makes the monoclinic phase fraction in the annealed samples from 9 to 20 mol % after 6 cycles.

Figs 4 and 5 show that in the alternating aging at 473 K in a saturated steam atmosphere and at 773 K in air, monoclinic phase fraction after the 473 K aging in the samples annealed at 773 K decreased with cycles, while it increased in the samples annealed at 1073 K.

The tetragonal to monoclinic phase transformation at 473 K is influenced by tetragonality [18]. It is supposed that the change of tetragonality in the plasma-sprayed coatings indicates the degree of residual stress relief. As shown in Figs 1–3, residual stress appears to remain in the samples annealed at both 773 K and 1073 K.

On the other hand, the tetragonal to monoclinic phase transformation at the 473 K aging occurs with volume expansion. Due to this volume expansion, it is supposed that stress is induced in the samples. From this point of view, it is suggested that the volume expansion by the $t \rightarrow m$ phase transformation by which the monoclinic phase fraction exceeded 50 mol % partially relieved the residual stress. It is suggested that this decrease of the stress makes the monoclinic phase fraction smaller with cycles after the 473 K aging in alternating aging.

It is also suggested that by the volume expansion due to the $t \rightarrow m$ phase transformation by which the monoclinic phase fraction did not exceed 20 mol %, the residual stress was accumulated. This increase of stress is probably the cause of the monoclinic phase fraction increase with cycles after the 473 K aging in alternating aging.

4. Conclusions

The phase transformations of the plasma-sprayed 6 mass % yttria-stabilized zirconia coatings in the alternating aging at 473 K in steam saturated atmosphere and at 773 K in air atmosphere was investigated, where the coatings had been annealed at 773 K and 1073 K. After the first aging at 473 K in the first cycle, the monoclinic phase fraction in the samples annealed at 773 K became greater than that in the samples annealed at 1073 K. In the samples annealed at 773 K, the decrease of the monoclinic phase fraction after the 473 K aging was observed at every cycle of aging. On the other hand, in the samples annealed at 1073 K, the increase of the monoclinic phase was observed. In the plasma-sprayed zirconia coatings annealed at 773 K, it is suggested that tetragonal to monoclinic phase transformation is suppressed by the strain relief due to volume expansion, while that in the coatings annealed at 1073 K, the tetragonal to monoclinic phase transformation at 473 K is accelerated by the strain accumulation.

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