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Thermal Spray Yttria-Stabilized Zirconia Phase Changes during Annealing

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Phase stability of thermal barrier deposits made from yttria partially stabilized zirconia (Y-PSZ) is a requirement for extended service lifetime. The response of Y-PSZ plasma-sprayed deposits to annealing at 1000, 1200, and 1400 °C with times from 1 to 1000 h has been evaluated using the Rietveld analysis of neutron diffraction data. Results show that the yttria concentration of the as-sprayed tetragonal zirconia component generally decreased with increasing annealing temperature and time. As the yttria content in the tetragonal phase approached a limiting concentration, about 3.5 mol.% of $YO_{1.5}$, the tetragonal phase transformed into monoclinic phase on cooling. An increase in monoclinic phase content was clearly observed after annealing for 24 h at 1400 °C and was nearly 35% after 100 h at 1400 °C. A similar trend was observed at 1200 °C for longer annealing times, with monoclinic phase formation beginning after 400 h. At 1000 °C, experimental times were not sufficient for monoclinic phase to form, although a decrease in the yttria concentration in the tetragonal phase was observed.

Keywords neutron scattering, phase composition, Rietveld analysis, yttria-stabilized zirconia

1. Introduction

High energy efficiency, reliability, and longer maintenance intervals are being demanded for today's thermal barrier coatings (TBCs), which are used to reduce the surface temperature and increase the lifetime of blades and other hot engine components. With turbine inlet temperatures as high as 1300 °C,[1] long-term thermal stability of TBCs is imperative.

Zirconia, the most commonly used material for plasma-sprayed TBCs, exists in three crystallographic phases: a low-temperature monoclinic phase, an intermediate-temperature tetragonal phase, and a high-temperature cubic phase.[2] The tetragonal-to-monoclinic phase transformation is a diffusionless, martensitic-type phase transformation, which is accompanied by a significant density change. Since this transition in TBCs generally results in cracking of the type that is detrimental for the properties of deposits, it usually must be avoided. The amount of monoclinic phase is one of the important indicators of coating quality—it has been found that larger amounts of monoclinic phase in the deposits lead to early failure during thermal cycling.[3]

The solid solution addition of one of several oxides, such as yttrium oxide (yttria), can stabilize the high-temperature cubic phase. However, these fully stabilized zirconia compositions are seldom used for TBCs, because they exhibit relatively poor cycling life.[4] Addition of lesser amounts of stabilizing oxide can result in the metastable retention of the tetragonal phase at room temperature when sufficient amounts of the stabilizing oxide are in solid solution with the tetragonal zirconia. Typical TBCs are in this partially stabilized regime, with yttria contents of about 8.7 mol.% $YO_{1.5}$ ($\sim$8% by mass), and consist of both cubic and tetragonal phases. According to the equilibrium phase diagrams[2,5,6] (Fig. 1), the yttria partially stabilized zirconia (Y-PSZ) used for TBCs should be a mixture of monoclinic and cubic phases at room temperature. However, the rapid solidification that occurs during the thermal deposition process maintains the yttria distribution of the initial powder in the tetragonal phase and results in significant retention of the metastable tetragonal phase at room temperature. However, Y-PSZ materials partition yttria between the tetragonal and cubic phases in accordance with the phase boundaries in the equilibrium phase diagram above 1200 °C, resulting in the production of yttria-depleted tetragonal zirconia, which can transform to the monoclinic phase on cooling to room temperature.[7,8]

Phase characterization of these materials has routinely been studied using x-ray diffraction (XRD). Prior work has shown that neutron scattering can be used to quantify the monoclinic, tetragonal, and cubic phase contents.[9,10] Neutron scattering is superior to XRD for phase analysis, especially because of its ability to separately analyze the tetragonal and cubic phases.[9,11] The superiority of neutron diffraction follows from the different nature of interaction of neutrons and x-rays with matter; whereas x-ray scattering is dominated by scattering from heavy atoms, the neutrons scatter nearly equally from both the cation and anion sublattices, resulting in more information about the structure of the material.

Because both tetragonal and cubic phase lattice parameters depend on solid solution yttria content, it is possible to establish the yttria concentration in each of these two phases and to observe the changes that occur in phase content and yttria concentration of the phases during processing of samples. The present work uses Rietveld analysis of neutron diffraction data to examine the phase composition and yttria content variations of Y-PSZ deposits. Rietveld refinement[12] is a technique in which the entire scattering pattern is fitted on the basis of a model that includes known crystallographic parameters (unit cell, atomic

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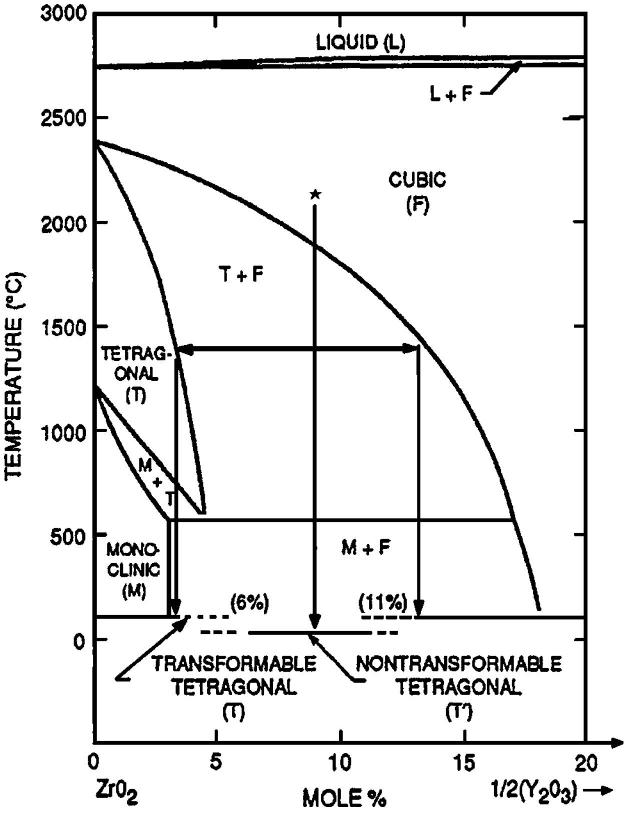

Fig. 1 Phase diagram of YSZ[5]

positions, *etc.*), as well as on pattern line shape, background, and phase composition. The model parameters are then adjusted *via* least-squares refinement. The unit cell parameters, atomic coordinates, thermal parameters, and powder line shape are refined independently. This technique can be used with either x-ray or neutron radiation, but has proven most successful with neutron powder diffraction owing to the symmetric peak shape, scattering at higher diffraction angles, and greater sensitivity to light atoms that are obtained with neutron radiation. These factors are of particular importance in the phase analysis of zirconia, because the diffraction peaks of the cubic phase are frequently not clearly separated from those of the tetragonal phase.

In the present work, the response of free-standing plasma-sprayed zirconia coatings to annealing at temperatures of 1000, 1200, and 1400 °C for times up to 1000 h was evaluated. The phase content and lattice parameters of annealed, as well as as-sprayed, samples were determined using Rietveld analysis of neutron diffraction data.

2. Experimental

Plasma-sprayed deposits were produced by the Plasma Technik, Sulzer-Metco (Wesbury, NY), PT F4[1] plasma-spray system. The feedstock material was Osram-Sylvania (Towanda, PA) SX233[1] ZrO_2-8% Y_2O_3 (mass fraction) with a size distribution from about 26 to 96 μm. This material was manufactured by the HOSP technique, a proprietary technique similar to plasma spheroidization. The powder was sprayed at a 90 mm spray distance with a feed rate of 26 g/min, using an 8 mm spray nozzle diameter, a 1.8 mm powder injector diameter, and a current of 500 A at 68 V. The argon primary gas flow was 40 L/min at standard temperature and pressure (slpm), with 10 slpm hydrogen secondary gas and 3 slpm argon carrier gas. To obtain the free standing samples used in this study, deposits of about 5 mm thickness were sprayed onto a mild steel substrate ($50 \times 25 \times 2.5$ mm), which had been coated with a layer of aluminum. After spraying, the Al layer was dissolved in 20% HCl to obtain free-standing deposits. A low speed diamond saw was used for sectioning the samples to dimensions of about $25 \times 5 \times 5$ mm.

Coating samples were annealed at 1000, 1200, and 1400 °C in air in a box furnace with $MoSi_2$ heating elements, with heating and cooling rates of 600 K/h. Annealing times ranged from 1 to 1000 h (1 to 200 h for the 1400 °C experiments).

Neutron diffraction data were obtained using the National Institute of Standards and Technology 32-detector high-resolution powder diffractometer. Data were collected over the range 5 to 165° 2θ, with a neutron wavelength of 1.5402(1) Å, the (1) indicating the estimated or measured standard deviation of the measured number on the last shown decimal place.

The data were then processed into a single-detector simulation and refined using the General Structure Analysis System (GSAS) suite of programs for structural analysis.[13] The overall background was fit using Chebychev polynomials. The data were analyzed using Rietveld analysis for the monoclinic, tetragonal, and cubic phases. For most of the plasma-sprayed coatings, the amounts of monoclinic phase present were too small to allow structural refinement of this phase, and the structural parameters were assumed to be the same as those determined for the few samples that exhibited significant amounts of monoclinic phase formation. The phase fraction of each of the three phases was also refined. The estimated standard uncertainties for the yttria concentrations in the tetragonal phase are about ±0.1%, and the uncertainties for the phase contents are about ±2%.

The calculation of yttria concentration (mole fraction in percent) within the tetragonal phase was based on changes in lattice parameters, as described by Scott[2] and modified as described elsewhere,[10] using the equation

$$YO_{1.5}(\text{mol.\%}) = \frac{1.0225 - \dfrac{c}{a\sqrt{2}}}{0.0016}$$

where c and a are lattice parameters of the tetragonal phase lattice.

This modification was necessary to maintain calculation of a constant value for the total $YO_{1.5}$ content in the coatings throughout the annealing process. The scaling factor of 0.0016 was calibrated from analysis of the feedstock material, using the chemical composition supplied by the manufacturer.

3. Results and Discussion

The changes in phase composition with annealing are given in Fig. 2, and the variations of average $YO_{1.5}$ concentration for

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[1] Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily best for the purpose.

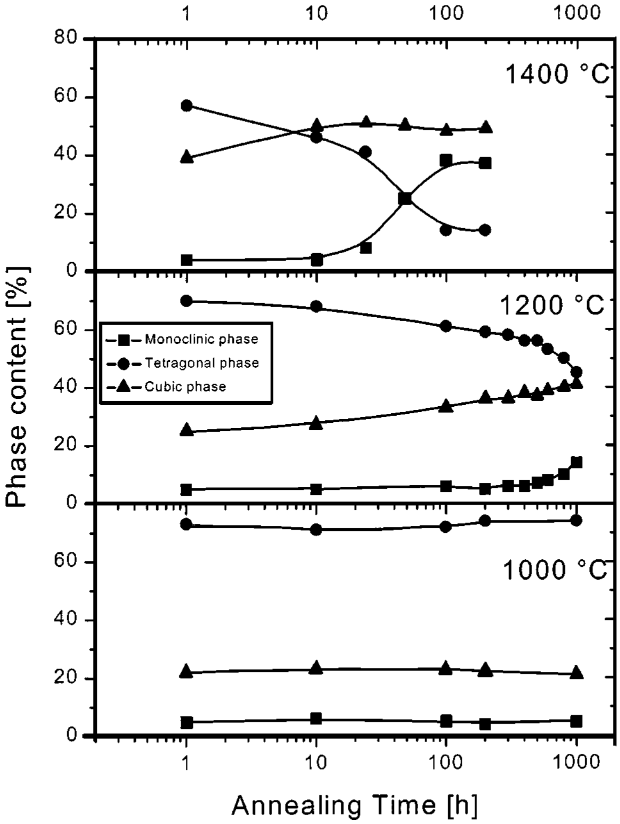

Fig. 2 Phase content variations during annealing

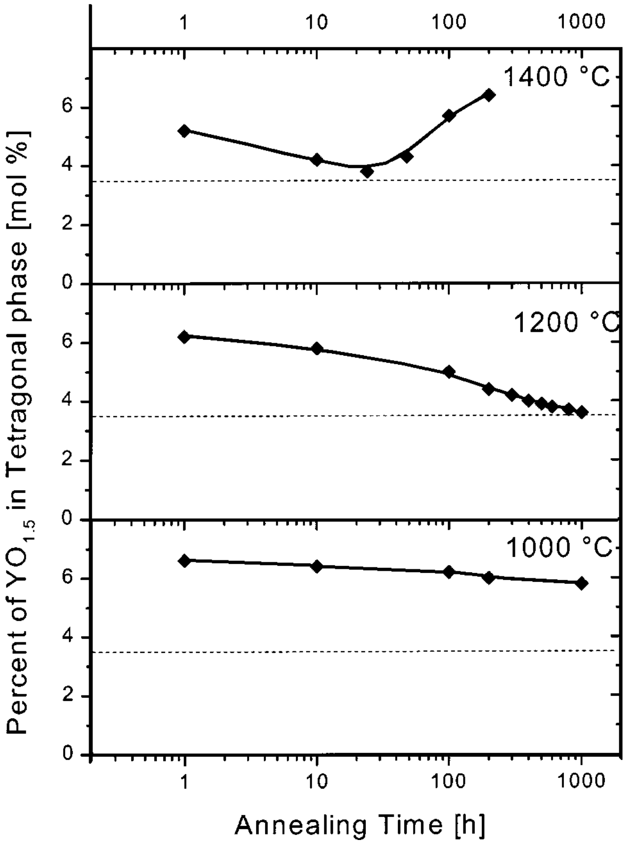

Fig. 3 Yttria content in the tetragonal phase. The dashed lines represent 3.5 mol.% $YO_{1.5}$, the approximate limit of stability for this material

the tetragonal phase are presented in Fig. 3. Uncertainties (±2% for phase composition and ±0.1% for $YO_{1.5}$ content) are omitted for the sake of clarity; smooth lines used to connect points in the figures are only to guide the eye and do not represent any calculated dependencies.

For the coatings annealed at 1400 °C for 100 h or longer, two distinct tetragonal phases were distinguished in the scattering pattern: one with a relatively low yttria content that decreased in the amount of phase present with longer annealing times, and one with a higher average yttria content. However, their reliable distinction is difficult. In this paper, these two phases are reported together, and, in Fig. 3, only the average yttria content is reported.

3.1 Cubic Phase

Annealing resulted in a decrease of yttria concentration in the tetragonal phase (Fig. 3) for all temperatures studied. No formation of free yttria phase was observed. Assuming that the total yttria content in the deposits did not change, this decrease of yttria concentration in the tetragonal phase must be compensated by an increase in the yttria concentration in the cubic phase, an increase in the cubic phase content, or a combination of both. A combination of both has been observed. For the samples annealed at 1000 °C, little change was observed in the overall phase content (Fig. 2). There was a slight increase in the cubic lattice parameter, a, with increased annealing time, with the value for a increasing from 5.1388(3) Å for the as-sprayed material to 5.1400(4) Å after 1000 h. Using the equation

$$YO_{1.5}\ (\text{mol.\%}) = (a - 5.1159)/0.001547$$

for yttria concentration of the cubic phase derived from the data of Scott,[2] this increase corresponds to a mole fraction of approximately 15% $YO_{1.5}$. For the samples annealed at 1200 °C, however, the cubic lattice parameter increased steadily and significantly with annealing time to a value of 5.1434(3) Å after 1000 h. This corresponds to a mole fraction of 18% $YO_{1.5}$ in the cubic phase and clearly shows a transfer of yttria from the tetragonal to the cubic phase. The situation is more complex for the coating samples annealed at 1400 °C, where relatively rapid phase changes occur (Fig. 2). In this case, the loss of yttria concentration in the tetragonal phase was balanced by an increase in the relative amount of cubic phase content, and the average $YO_{1.5}$ concentration in the cubic phase remained constant at about 14%.

3.2 Tetragonal Phase

The process of destabilization of the tetragonal phase and the yttria concentration limit at which this destabilization occurs can be observed in the results for samples annealed at 1400 °C. With increasing annealing time up to about 24 h, the $YO_{1.5}$ concentration in the tetragonal phase decreased to below 4%. Formation of monoclinic phase at this yttria level suggests that the stability limit of the tetragonal phase is reached near this yttria composition. Further annealing resulted in an increase of the monoclinic phase content up to about 35% for an annealing time of 100 h. The increase in the overall yttria concentration in the tetragonal phase during the monoclinic phase formation is related to the existence of two distinct maxima for yttria concentration in the tetragonal phase, as previously discussed. The monoclinic phase is formed from tetragonal phase with lower yttria concentration, and the yttria-richer areas remain. This disappearance of low yttria areas results in an increase in the average yttria concentration of the remaining tetragonal phase.

A similar clear trend of decreasing yttria concentration in the tetragonal phase is observed at 1200 °C. At this temperature, the end of stability of the tetragonal phase is reached after around 400 h annealing. Because the processes at this temperature are slower, it is possible to estimate more precisely the yttria content at which the increase in monoclinic phase is observed (*i.e.,* the limit of stability of the tetragonal phase). It appears that, for this material, this limit of stability is about 3.5% $YO_{1.5}$. However, the actual yttria content of the material that undergoes the tetragonal-to-monoclinic phase transition may be lower, since the broad diffraction peaks that are observed are most likely due to the existence of a range of yttria concentration. As discussed previously, an associated increased yttria concentration in the residual cubic phase is also observed.

At 1000 °C, the decrease of yttria concentration in the tetragonal phase can also be observed. However, a decrease significant enough to result in destabilization of the tetragonal phase will probably occur at annealing times much longer than those used in the current study.

3.3 Use of X-rays for Analysis

The phase composition of TBCs is of fundamental importance to the prediction of coating stability, and, furthermore, the yttria concentration of the tetragonal phase serves as an indicator of potential tetragonal phase destabilization. However, the practical engineering tool for phase composition studies is XRD, not neutron scattering. Also, Rietveld analysis, while a routinely accepted technique in academic research, may be cumbersome in engineering practice. Therefore, it is necessary to find a more accessible way to determine how to apply the findings of this study in engineering practice. Several methods for XRD phase composition studies of YSZ materials were evaluated. The results show that even Rietveld analysis of XRD data may not necessarily yield precise results. In part, this is due to problematic peak shape definition, which is an integral part of the Rietveld analysis, when tube-based XRD equipment is used, in addition to the factors mentioned earlier.

The value of the tetragonal *a* lattice parameter, as evaluated from the XRD peak positions directly or by application of the Rietveld method, is the best practical tool for determination of the yttria concentration of the tetragonal phase. Using the relationship

$$YO_{1.5}\ (\text{mol.\%}) = (a - 3.5963)/0.00227$$

given by Toraya,[14] the yttria concentration in the tetragonal phase can be determined to within about 0.5 mol.%. Relative changes in the yttria content are reproduced more precisely. The tetragonal *c* lattice parameter is often difficult to determine accurately due to overlap with the cubic diffraction peaks, and thus the *c/a* ratio is of little use for calculation of yttria concentration using XRD data. As the samples are annealed and the yttria concentration of the tetragonal phase decreases, the separation of the tetragonal and cubic XRD peaks increases, and the determination of both *a* and *c* is facilitated. However, the use of the *a* lattice parameter alone is preferred for the concentration range of interest.

4. Conclusions

Current operational temperatures of turbines are reaching the point at which the TBCs manufactured from yttria-stabilized zirconia will no longer be able to serve for prolonged times. The results of this study show that the stability of the Y-PSZ thermally sprayed TBCs may be too low for long-term use at temperatures around 1200 °C; significant transformation of the tetragonal-to-monoclinic phase occurred after about 400 h of annealing. At 1400 °C, the stability of the deposits was compromised after only 24 h of annealing.

These results also show that the yttria concentration in the tetragonal phase can be used as an inspection tool to predict the degree of destabilization of the Y-PSZ TBCs. The limit found in this work is about 3.5% $YO_{1.5}$. If coated engine parts can be inspected during engine maintenance, the phase stability and therefore the potential failure due to Y-PSZ destabilization can be evaluated. The proposed method for calculating the yttria content in the tetragonal phase using standard XRD laboratory equipment presents the possibility of routine phase stability evaluation of parts during engine refurbishment. However, it is necessary to understand that lifetime prediction for TBCs is a complex problem, of which the phase stability is only part. Other effects, such as strain accumulation, oxidation of bond coat, and sintering and related microstructural changes, also play important roles.

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