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Sol infiltration and heat treatment of alumina–chromia plasma-sprayed coatings

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Abstract

Alumina–chromia coatings deposited on alumina substrates by plasma spraying were subjected to various combinations of thermal and chemical treatments in an attempt to improve their high-temperature stability. The chemical treatment consisted of infiltrating the coatings with a SiO_2-containing sol. The thermal treatments involved subjecting the coatings to thermal cycles in a furnace prior to and following the infiltration. Observation of the microstructure of these samples revealed that the introduction of silica, which reacted with alumina to produce mullite during heat treatment, reduced cracking within the coating and between the coating and substrate. Crown Copyright © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Al_2O_3–Cr_2O_3; Coatings; Plasma spraying

1. Introduction

Plasma-sprayed ceramic coatings are often used for protecting surfaces against various types of adverse environments involving high temperatures, wear and corrosion, which can degrade the underlying component. For applications under conditions at or near room temperature, such as might be the case in some situations requiring wear resistance or be found in corrosive marine environments, the operating temperature may not play a major role in affecting the stability of the microstructure of the coating. However, for high-temperature applications where ceramic coatings may serve as thermal barriers or as protection against attack by corrosive species such as liquid metal, the elevated temperature can cause phase transformations, densification, cracking and ultimately, fragmentation and debonding of the coating.

Alumina coatings produced by thermal spraying have been shown to undergo changes that alter both the phase composition and microstructure of the coating when heated to temperatures in the range of 1000–1200°C.[1–7] The changes arise due to the initial formation of metastable γ-alumina in the coating, owing to the rapid solidification of the molten particles upon impacting the substrate, and the subsequent series of phase transformations that lead to the production of the stable α-alumina phase when the coatings are heated to temperatures up to 1200°C. These changes may be acceptable when plasma spraying is being used to produce bulk alumina components (spray forming). In this case, the substrate is removed so that the coating is not constrained from expanding or contracting during heat treatment. However, for situations in which the coating is to remain on the component and be used at high temperatures, the phase transformations and sintering can lead to fragmentation and spalling of the coating.

It has been reported that the addition of Cr_2O_3 can have a positive effect on the stability of plasma-sprayed alumina-based coatings.[5,8–10] However, while the presence of Cr_2O_3 can help to limit the phase transformations that occur during heat treatment at temperatures below 1200°C, cracking, debonding and fragmentation of the coating can still occur due to sintering stresses generated at higher temperatures.

Research on producing mullite–alumina composites by infiltration processing has demonstrated that the introduction of SiO_2 into porous alumina compacts can retard the onset of densification when these infiltrated bodies are exposed to high temperatures.[11] Those results

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suggest that there may be some potential for using a similar approach to stabilize plasma-sprayed alumina-based coatings for use at high temperatures. Infiltration of thermal spray coatings has been used in the past, and, recently, the feasibility of using sol–gel infiltration as a way of sealing plasma-sprayed thermal barrier coatings was demonstrated.[12] The present paper provides preliminary results of a study to determine the effect of SiO_2 sol infiltration on the high temperature stability of plasma-sprayed Al_2O_3-Cr_2O_3 coatings. The research was performed as part of a larger study aimed at developing acoustic wave guides for use in liquid metals at elevated temperatures.[13,14]

2. Experimental procedure

2.1. Processing

Plasma-sprayed coatings were produced from a 20 mol% Cr_2O_3–Al_2O_3 powder (Trans-Tech, Inc., Adamstown, MD) by depositing a layer approximately 300 μm thick onto dense alumina rods or disks (AD-998, Coors Ceramics Co., Golden, CO) using a high power plasma spray system (Axial III, Model 550, Northwest Mettech Corp., Richmond, BC, Canada). The surfaces of the ceramic samples were roughened by grit blasting with an alumina grit (no. 24 grit size) before depositing the coatings. The torch was operated at a current of 200 A and a power level of 80 kW using a plasma gas flow of 120 l/min of a 10% Ar–10% H_2–80% N_2 gas mixture. The powder feed rate was 11 g/min using argon as the carrier gas. An air jet directed onto the surface of the samples was used to cool the substrates during spraying. Periodic measurements at the surface of the deposit using a contact thermocouple indicated that the temperature did not exceed 220°C.

Some of the coated samples were then subjected to a thermal cycle by heating them in air at a rate of 5°C/min to 800, 1000, 1200 or 1550°C. The samples were held for 2 h at the maximum temperature, at which point the power was turned off and the samples left to cool in the furnace (reaching room temperature after several hours). Infiltration of several of the coatings was performed by completely immersing the coated samples in an ethyl silicate solution (R-25, Remet Chemical Corp., Chadwicks, NY) containing 25% by weight of SiO_2. No attempt was made to accelerate or enhance the rate or degree of infiltration by using a vacuum to remove air from the pores prior to immersion or by applying pressure to force the liquid into the pores. Following a 24-h immersion, the samples were removed, allowed to dry in air at room temperature for at least 24 h and then heated to 600°C at 1°C/min to decompose the ethyl silicate. This slow rate was used to provide sufficient time for any gaseous products to escape and thereby avoid damaging the coating, which could occur if there was a build-up in pressure due to entrapped gas. The decomposition characteristics of the infiltrant have been discussed elsewhere.[15] A final heat treatment was performed at 1550°C, a temperature considered sufficiently high to result in the formation of mullite.[15]

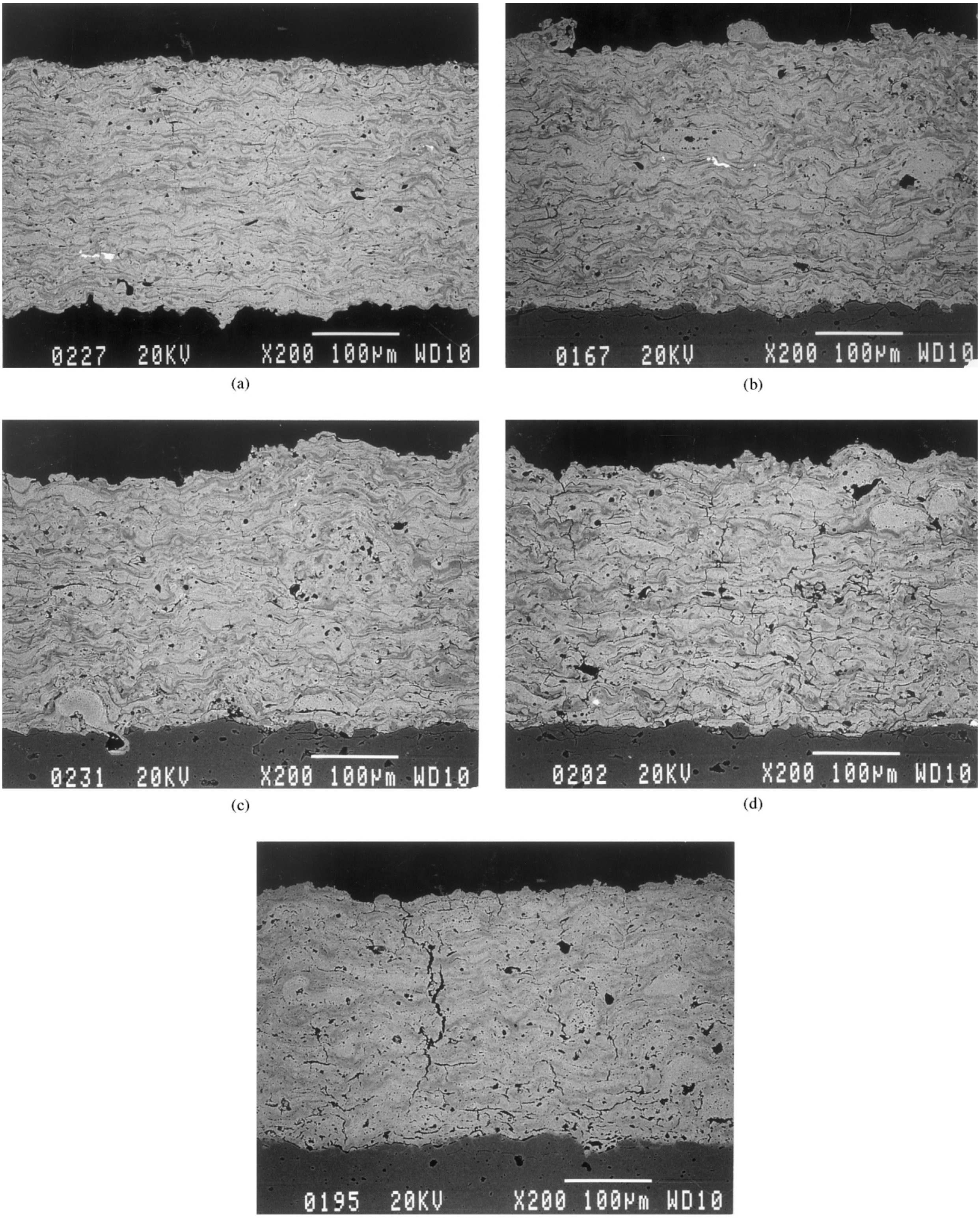
2.2. Analyses

The coatings deposited on flat disks were analyzed using X-ray diffraction (XRD) to determine the phase composition at different stages of processing. Several of the coated samples were embedded in an epoxy resin, sectioned, and polished in order to study the microstructure. The mounting procedure involved a vacuum impregnation during which the samples were first placed in a container under vacuum to remove the air, then covered with an epoxy [Caldofix (resin and hardener), Struers, Copenhagen, Denmark] while still under vacuum and, finally, exposed to atmospheric pressure to aid the impregnation process. The epoxy was cured by placing the samples in an oven at 80°C for a 2-h heat treatment. The mounted samples were sectioned using a diamond saw to cut in the direction from coating through to the substrate, so as to keep the coating under compression. The polishing procedure was performed using a series of diamond pastes and terminating in a final step using 0.05 μm alumina dispersed in demineralized water. The goal in all of these steps was to retain the true microstructure and not introduce artifacts (cracks, debonding, grain pullout, etc.) due to the use of incorrect mounting, cutting or polishing procedures. Analysis of the microstructure was performed using a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS), which was used for determining the distribution of Si in the coatings.

3. Results and discussion

3.1. Effect of heat treatment on coatings

The microstructures of Al_2O_3–Cr_2O_3 coatings that had been deposited on alumina disks and exposed to various heat treatments are shown in Fig. 1. These coatings had not been subjected to infiltration. Differences in the degree of cracking present in the samples can be observed. For the as-sprayed sample and the samples heated to 800 and 1000°C, very few cracks could be observed at the magnification used for the micrographs shown in Fig. 1. However, after heating a coated sample at 1200°C, vertical cracks became evident, as shown on the microgragh in Fig. 1d. Additional heating of the coating to 1550°C caused further changes. While some of the vertical cracks observed in coatings heated to 1200°C disappeared, some major cracks appeared. In



(a) (b)

(c) (d)

(e)

Fig. 1. Micrographs of Al_2O_3–Cr_2O_3 coatings at various stages of heat treatment prior to infiltration: (a) as-sprayed, (b) 800°C, (c) 1000°C, (d) 1200°C, and (e) 1550°C.

some cases these were visible to the naked eye. Preliminary measurements appeared to indicate that the level of porosity present in the coatings increased with temperature for the heat treatments up to 1200°C and then decreased in the samples heated to 1550°C, presumably due to the onset of sintering leading to densification.

Results of the XRD analyses for the various coatings as well as the starting powder are shown in Fig. 2. These spectra indicate that the starting powder consisted of a solid solution of Al_2O_3–Cr_2O_3, principally present in the α phase but also containing a small amount of the γ form. The as-sprayed coating also contained the α form of alumina as the major constituent; however, there also appeared to be some γ phase present, as indicated by the $(400)_\gamma$ lines in the vicinity of 45°.

Heat treatment of these coatings produced only small changes in the phase composition. Traces of δ alumina were detected following heating at 800 and 1000°C. In the coatings heated at 1200 and 1550°C only the α phase was detected. No attempt was made to use this analysis to determine quantitatively the phase composition of the coatings. These results are similar to those reported in an in-depth study by Chráska et al.[6] in which coatings produced using a water-stabilized plasma gun were subjected to various heat treatments and then analyzed.

3.2. Combined effect of infiltration and heat treatment on coating integrity

Fig. 3 shows the microstructures of three coatings that had been deposited on half-inch diameter alumina rods, subjected to a heat treatment (Fig. 3b and c), infiltrated with a silica-containing sol, and, finally, heated to 1550°C. The infiltration treatment appeared to reduce the degree of cracking induced in the coatings when the samples were heated to 1550°C (compare to Fig. 1e). The serious cracks observed in samples that had not been infiltrated prior to this type of heat treatment were absent from the infiltrated coatings. It also appeared that the coating subjected to a heat treatment at 1000°C prior to infiltration had fewer cracks than the other two coatings; however, no attempt was made to quantify the degree of cracking in the various coatings.

It was also observed that the bonding between the coating and substrate appeared to be affected by this treatment. This can be seen in Fig. 4 where the substrate–coating interface region is shown for coated rods that had been subjected to various treatments. For the as-sprayed coating (Fig. 4a), a fine crack can be observed along much of the interface. When such a sample was heated to 1550°C, a gap of several micrometers opened between the coating and substrate (Fig. 4b). Conversely, for the sample that was infiltrated before heating to

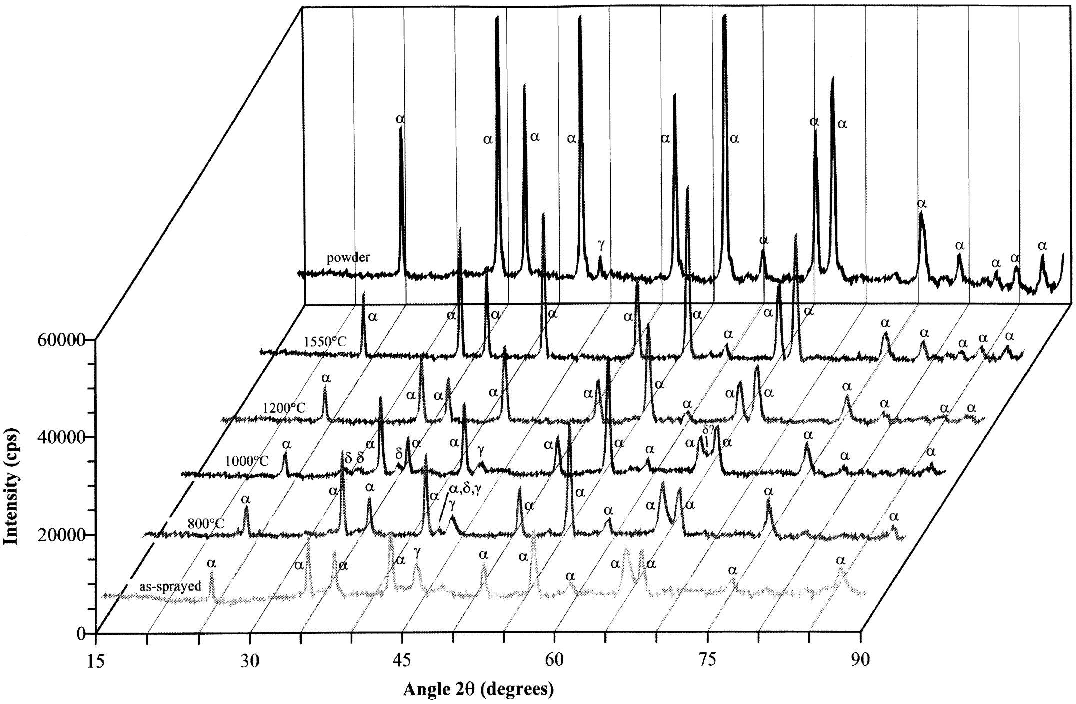
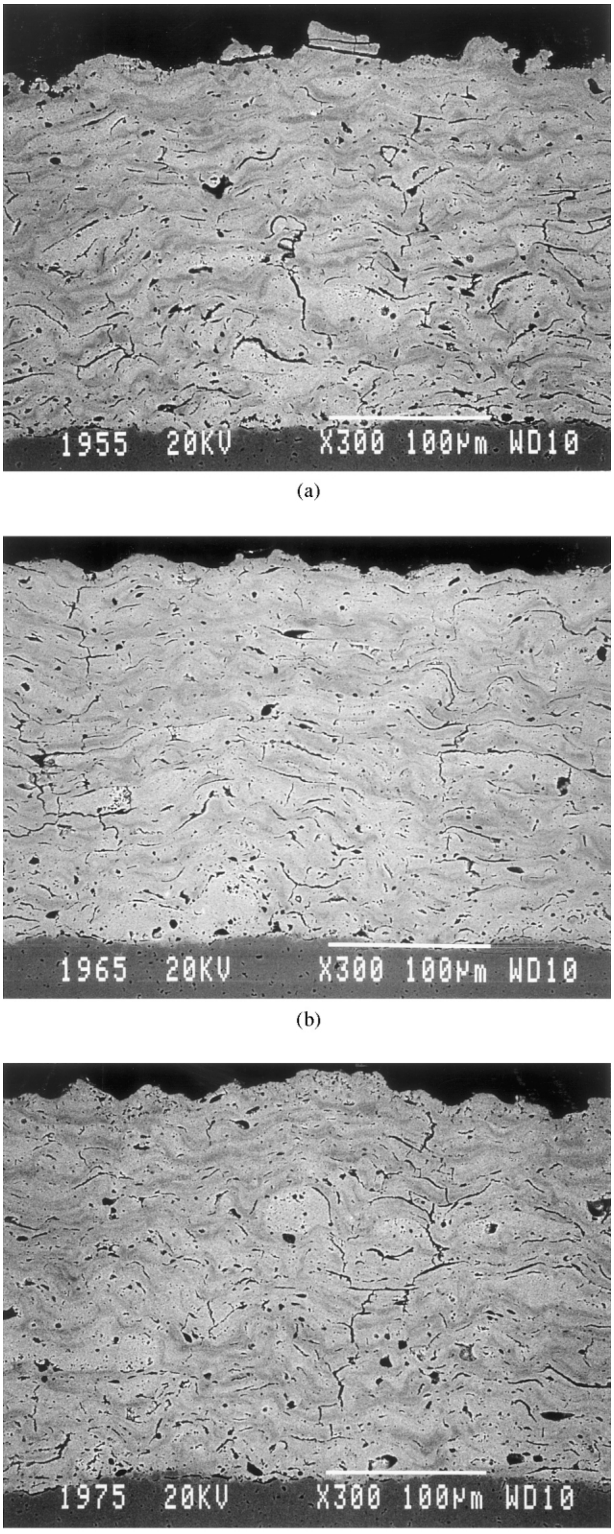


Fig. 2. X-ray diffraction spectra of the starting Al_2O_3–Cr_2O_3 powder, the as-deposited coating, and the coatings after a heat treatment at 800, 1000, 1200 or 1550°C.

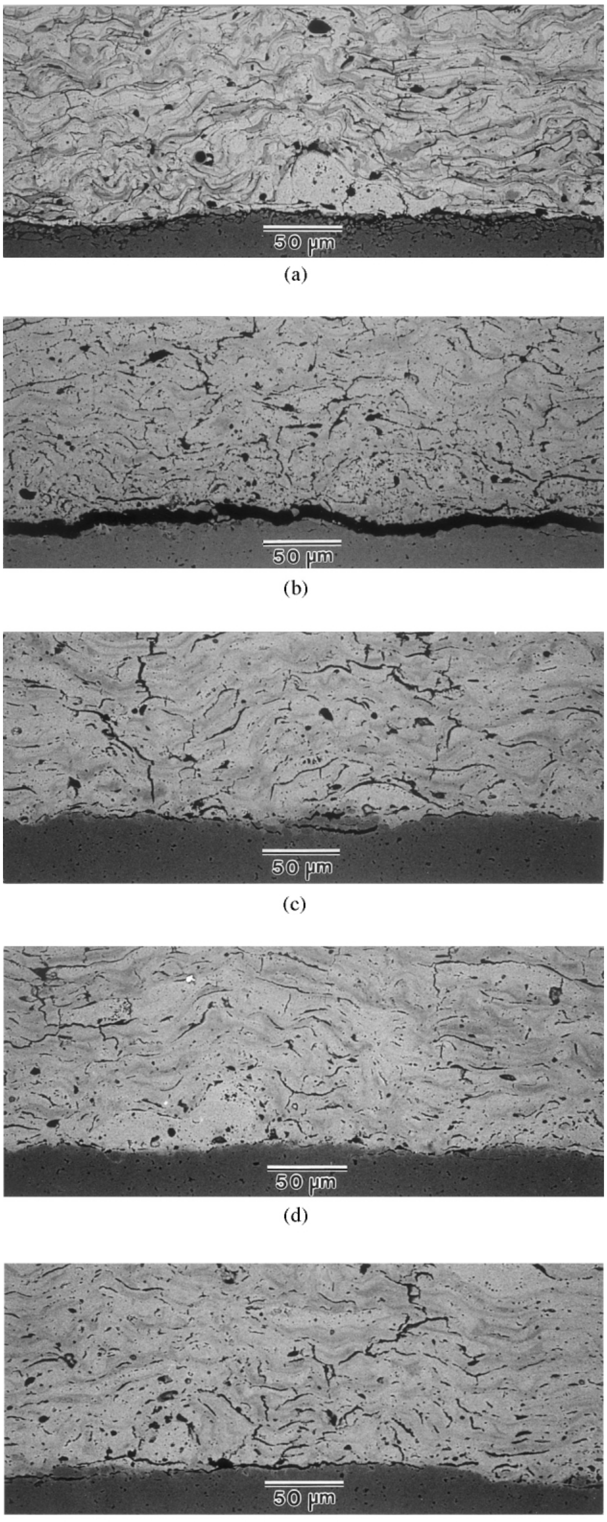


(a)

(b)

(c)

Fig. 3. Micrographs of infiltrated coatings following a final heating to 1550°C. The pre-infiltration treatment of the samples was as follows: (a) as-sprayed, (b) heat treatment at 1000°C and (c) heat treatment at 1200°C.



(a)

(b)

(c)

(d)

(e)

Fig. 4. Micrographs of the interface region of samples submitted to the following conditions of initial heat treatment/infiltration/final heat treatment: (a) none/none/none (as-sprayed), (b) none/none/1550°C, (c) none/24 h/1550°C, (d) 1000°C/24 h/1550°C, and (e) 1200°C/24 h/1550°C.

1550°C, the severity of the interface crack had noticeably lessened following heat treatment (Fig. 4c). For the samples that had been subjected to heat treatment prior to infiltration and heating to 1550°C, the effect was even more pronounced (Fig. 4d and e). This was particularly true for the sample heated to 1000°C before infiltration. In this case, the interface crack was almost completely healed to produce what appeared to be a well-bonded coating and a clean interface (Fig. 4d).

The distribution of Si through a cross section of the sample that had been heated to 1000°C, infiltrated with SiO_2 and then heated to 1550°C is shown in Fig. 5. It can be observed that the Si is located at the surface of the coating, within the coating in areas associated with cracks or, perhaps in some cases, with former cracks, and at the interface between the coating and substrate. The global SiO_2 content of this coating, as determined using EDS analysis, was found to be 1.5% in terms of the mass. A similar value was obtained for the SiO_2 present in the other two coatings (Fig. 4c and e) that had a different thermal history prior to infiltration.

X-ray diffraction analysis of the coatings shown in Fig. 4c–e is presented in Fig. 6. These spectra provide evidence of the presence of mullite in the coating, indicating that, during the thermal cycle to 1550°C, silica and alumina had reacted to form this new phase in infiltrated samples. No attempt was made to determine the amount of mullite present using XRD analyses. However, if all the SiO_2 present in the samples, as determined by EDS analysis, is in the form of stoichiometric mullite, then based on the mullite formation reaction,

$$3Al_2O_3 + 2SiO_2 \Longleftrightarrow 3Al_2O_3{\cdot}2SiO_2, \qquad (1)$$

the amount of mullite present could be estimated at 5%.

The reaction of silica with alumina could serve to lessen the severity of cracks within the coating and, because the substrate also consisted of alumina, to improve bonding between the coating and substrate. This could occur if the SiO_2 that had infiltrated to the interface region reacted with the alumina on both sides of the interface (coating and substrate). The infiltration/heat treatment will tend to partially fill the porosity by, initially, introducing SiO_2 and, subsequently, through a volume expansion of approximately 4% when the SiO_2 (in the form of cristobalite) reacts with α-Al_2O_3 to form mullite. As mentioned above, the presence of SiO_2 and mullite retards the onset of densification of alumina.[11] In the present case, this can be beneficial in limiting the sintering of the coating and reducing the stresses associated with the shrinkage of the coating attached to a fully dense substrate.

The potential for increased bonding due to the reaction of SiO_2 with the alumina within the coating and at the interface and the role that the presence of SiO_2 can play in retarding densification and decreasing shrinkage can all contribute to reducing the amount of cracking that occurs during heat treatment. Further investigation is required in order to more precisely evaluate the level of porosity in samples at various stages of the process, measure the amount of SiO_2 introduced and determine the extent of mullite formation. Additional work is also required in order to quantify the effect of the process on the cohesive strength of the coating and on the bond between the coating and substrate. However, the results of the present study demonstrate that by tailoring the chemical composition and thermal treatment of alumina-based plasma-sprayed coatings, evolution in the interfaces within the coating and at the coating-substrate boundary during heat treatment up to 1550°C can be significantly affected.

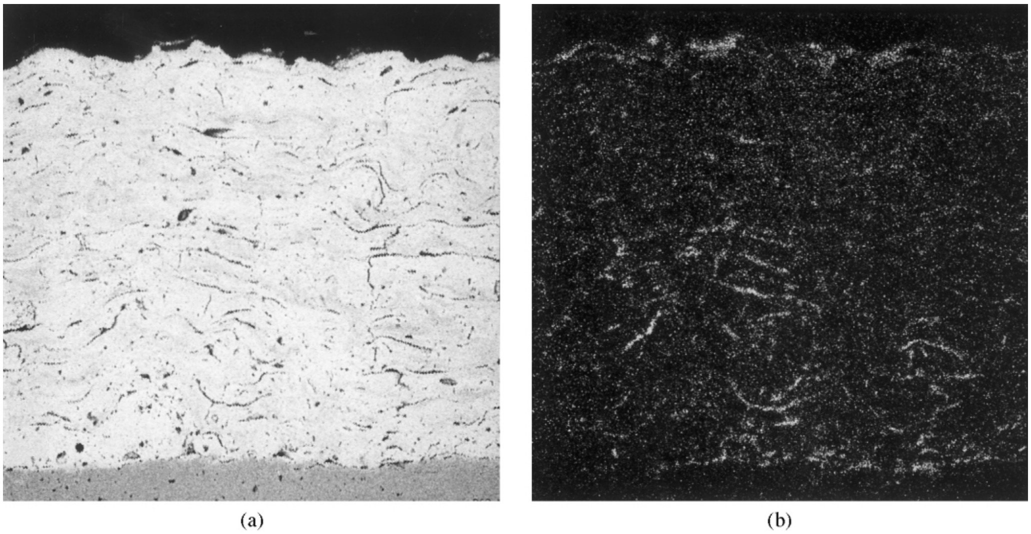

(a) (b)

Fig. 5. Backscattered electron image (a) and an EDS X-ray dot map for silicon (b) for a sample that had been heat treated at 1000°C prior to infiltration and final heating to 1550°C.

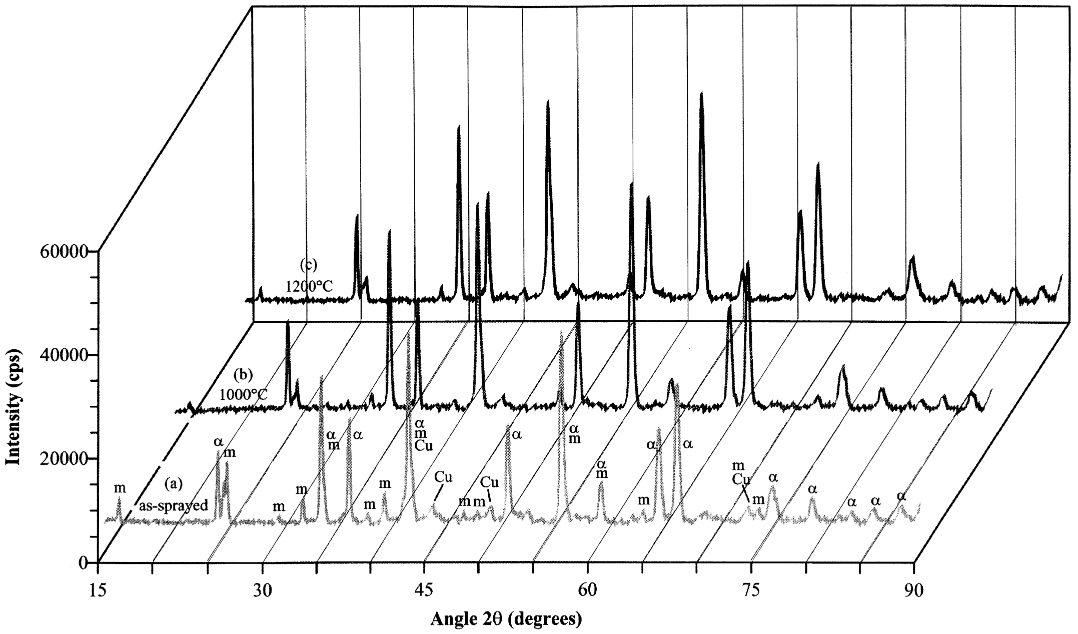


Fig. 6. X-ray diffraction spectra for three coatings that had been infiltrated with a silica-containing sol and then heated to 1550°C. The peaks are identified as belonging to mullite (m), alpha-alumina (α) or the copper (Cu) mask used to hold these samples during the analysis. The thermal treatment of samples prior to infiltration was as follows: (a) no heat treatment (as-sprayed), (b) heated to 1000°C and (c) heated to 1200°C.

3. Summary

The infiltration of plasma-sprayed Al_2O_3–Cr_2O_3 coatings with a silica-containing sol resulted in a significant reduction in cracking at the interface between the coating and the alumina substrate following heat treatment at 1550°C. It was also observed that this infiltration treatment lessened the severity of cracking within the coating when heated to high temperatures. It has been shown that this combined chemical (infiltration with SiO_2) and thermal (heating to 1550°C) treatment leads to formation of mullite through the reaction of silica and alumina. Tests on determining the effectiveness of subjecting the coated samples to a heat treatment prior to infiltration appeared to indicate that samples treated at 1000°C exhibited better-bonded coatings having fewer cracks. These preliminary results point to the potential of using this approach to induce crack healing in coatings, increase bonding between the coating and substrate, and improve the high temperature stability of coating–substrate couples.

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References

1. Thompson, V. S. and Whittemore, O. J. Jr., Alumina-base plasma-sprayed materials Part I, Structural changes on reheating plasma-sprayed alumina. *Am. Ceram. Soc. Bull.*, 1968, **47**(7), 637–641.
2. Hurley, G. F. and Gac, F. D., Structure and thermal diffusivity of plasma-sprayed Al_2O_3. *Am. Ceram. Soc. Bull.*, 1979, **58**(5), 509–511.
3. Lima, R. S. and Bergmann, C. P., Structural changes on post-sintered flame-sprayed alumina and alumina-titania. In *Advances in Thermal Spray Science and Technology*, ed. C. C. Berndt and S. Sampath. ASM International, Materials Park, OH, 1995, pp. 327–332.
4. Lima, R. S. and Bergmann, C. P., Phase transformations on flame-sprayed alumina. In *Thermal Spray: Practical Solutions for Engineering Problems*, ed. C. C. Berndt. ASM International, Materials Park, OH, 1996, pp. 765–771.
5. Chráska, P., Dubský, J., Neufuss, K. and Písacka, J., Alumina-base plasma-sprayed materials part I: phase stability of alumina and alumina-chromia. *J. Therm. Spray Technol.*, 1997, **6**(3), 320–326.
6. Ilavsky, J., Berndt, C. C., Herman, H., Chráska, P. and Dubský, J., Alumina-base plasma-sprayed materials — part II: phase transformations in aluminas. *J. Therm. Spray Technol.*, 1997, **6**(4), 439–444.
7. Damani, R. J. and Makroczy, P., Heat treatment induced phase and microstructural development in bulk plasma sprayed alumina. *J. Eur. Ceram. Soc.*, 2000, **20**, 867–888.
8. Dubský, J., Brozek, V., Kolman, B. and Chráska, P., Stabilization of α-Al_2O_3 plasma sprayed coatings by chromia. In *Proceedings of the International Ceramic Conference AUSTCERAM 92*, vol. 2, ed. M. J. Bannister. CSIRO, Australia, 1992, pp. 793–797.

9. Dubský, J., Kolman, B. and Chráska, P., Stability of alpha phase in alumina-chromia plasma sprayed deposits after annealing. In *Proceedings of the 7th National Thermal Spray Conference, Thermal Spray Industrial Applications*, ed. C. C. Berndt and S. Sampath. ASM International, Materials Park, OH, 1994, pp. 779–782.
10. Chráska, P. and Dubský, J., Alumina based plasma sprayed materials. In *Thermal Spraying: Current Status and Future Trends*, ed. A. Ohmori. High Temperature Society of Japan, Osaka, 1995, pp. 495–500.
11. Marple, B. R. and Green, D. J., Mullite/alumina particulate composites by infiltration processing: II, Infiltration and characterization. *J. Am. Ceram. Soc.*, 1991, **73**(12), 3611–3616; Correction, *ibid*., **74**(3), 641
12. Troczynski, T., Yang, Q. and John, G., Post-deposition treatment of zirconia thermal barrier coatings using sol-gel alumina. *J. Therm. Spray Technol*., 1997, **6**(4), 439–444.
13. Marple, B. R., Jen, C.-K. and Voyer, J., Ceramic-clad ceramic system for ultrasonic wave guidance. In *Thermal Spray: Meeting the Challenges of the 21st Century*, ed. C. Coddet. ASM International, Materials Park, OH, 1998, pp. 1109–1114.
14. Voyer, J., Marple, B. R. and Jen, C.-K., Plasma-sprayed ceramic coatings for ultrasonic wave guidance in severe environments. In *Proceedings of the United Thermal Spray Conference, UTSC'99*, ed. E. Lugscheider and P. A. Kammer. DVS — German Welding Society, Düsseldorf, Germany, 1999, pp. 630–635.
15. Marple, B. R. and Green, D. J., Mullite/alumina particulate composites by infiltration processing. *J. Am. Ceram. Soc*., 1989, **72**(11), 2043–2048.