Microstructural Characterization of Plasma-sprayed Oxide Ceramics

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Microstructural and microchemical characterization has been carried out on plasma-sprayed zircon (ZrSiO₄) and alumina-chromia (Al₂O₃-50wt%Cr₂O₃) by transmission electron microscopy and energy dispersive X-ray analysis. The as-sprayed zircon coatings consist of zirconia and silica glass as a result of phase separation during rapid cooling in the plasma-spraying process. Zirconia shows a tetragonal structure for small particles and a monoclinic for large particles. The zircon coatings annealed at 1300°C for 96 h in air show a mixture of zircon and monoclinic zirconia phases. Alumina-chromia coatings plasma-sprayed with N₂ gas consist mainly of a polycrystalline alumina-chromia solid solution with a typical grain size of 0.4 μm. Fine precipitates are observed frequently along the grain boundaries in the coatings sprayed with Ar–H₂ gas mixture or N₂–H₂ gas mixture. The fine precipitates are a metallic Cr-rich Cr–Al alloy formed by reduction of Cr₂O₃ and Al₂O₃ during the plasma-spraying process. These precipitates disappear during annealing at temperatures higher than 1300°C for 96 h in air. The precipitates affect the wear resistance of the coatings.

KEY WORDS: plasma spraying; ceramic coating; zircon; alumina–chromia; microstructure; transmission electron microscopy; wear resistance.

1. Introduction

Ceramic coatings are currently under active development in order to improve the static and dynamic strength of machine parts at high temperatures. Plasma spraying is one of the most common techniques to coat a wide range of different materials onto various substrates. The plasma-sprayed oxide coatings produce excellent properties of thermal barrier, wear resistance and corrosion resistance.

Recently in the steel making process a continuous annealing system has been developed to produce a wide variety of high quality cold-rolled steel sheets. It is necessary to reduce wear of hearth rolls in the system in order to improve the quality of steel sheets. It is also necessary to eliminate adhesion of iron and/or iron oxide powders to the hearth roll, because it makes scratches on the surface of the sheet. Ceramic coatings have been applied to the hearth rolls in order to cope with these demands. Several types of ceramic coatings have been examined; zircon coatings and alumina–chromia coatings are found to have both excellent wear resistance and low chemical reactivity with iron oxides.¹

Plasma spraying is a well-accepted technological process, however only a few careful studies have been done on the microstructural characterization with transmission electron microscopy (TEM). Plasma spraying yields characteristic microstructures obtained by rapid solidification. Thus metastable phases are frequently retained in the coatings. Thermal stability of the metastable phases is of interest both from metallurgical and practical points of view. This paper describes the results obtained by TEM study on the microstructures of plasma-sprayed zircon and alumina–chromia coatings and the microstructural changes of these coatings during subsequent high temperature annealing. Correlation between the wear resistance and the microstructure is also analyzed.

2. Experimental

2.1. Materials and Coating Procedure

Commercially prepared zircon (ZrSiO₄) powders and fused alumina–chromia (Al₂O₃-50 wt% Cr₂O₃) powders were used as the starting material for ceramic coatings. Plasma-spraying was carried out by a Meteco 7MB type torch with spraying parameters given in Table 1. Nitrogen gas was used as a plasma-forming gas: for fused alumina–chromia powders Ar–H₂ or N₂–H₂ gas mixture was also used. For the specimens subjected to the wear test, a metallic bond coating (CoCrAlY) and an intermediate coating (a mixture of CoCrAlY and ceramic powders) were deposited by plasma spraying onto SUS304 stainless steel substrates. For microstructural observation by TEM, specimens of ceramic coatings were prepared without the bond coating and the intermediate coating.

2.2. Wear Test

Wear test was performed with a ball-disc apparatus as shown in Fig. 1. A load of 10 kgf was applied during the wear test while the specimen rotated at a speed of 70 rpm. Wear volumes were measured for steel balls by an optical microscope and for plasma-
sprayed coatings by a surface roughness-measuring equipment.

2.3. Phase Analysis
X-ray diffractometry (XRD) with Cu Kα radiation was used to characterize the plasma sprayed ceramic coatings. The ceramic coatings were mechanically removed and ground to powder by an agate mortar and pestle. [111] reflections were analyzed to determine the ratio of the monoclinic zirconia to the tetragonal and cubic zirconia formed in the plasma-sprayed zirconia coatings.

2.4. Microstructural Observation
The ceramic coatings were mechanically removed from the substrates. Some coatings were annealed at temperatures higher than 1000°C in air. The coatings were polished with SiC papers and thinned to electron transparency with 5 kV argon ions. The morphology of the phases in ceramic coatings was analyzed by TEM imaging and diffraction techniques in a JEOL JEM-2000FX, a JEOL JEM-4000FX equipped with a Tracer Northern TN-5500 energy dispersive X-ray (EDX) analyzer and a Hitachi H-800 with a Kevek Micro-X 7000 EDX analyzer.

3. Results and Discussion
3.1. Characteristics of Plasma-sprayed Ceramic Coatings
Properties of plasma-sprayed coatings are listed in Table 2. The alumina–chromia coatings are found to be superior to the zircon coatings in terms of the Vickers hardness and the specific wear rate. Among the alumina–chromia coatings the specimens prepared in N₂ gas as plasma-forming gas show most excellent properties of hardness and wear resistance. Such differences in the properties are not apparently corre-

lated to the pore volume in the oxide coatings.

Phase analysis with XRD showed that the tetragonal and monoclinic zirconia and a trace of zircon were contained in the zircon coating. The ratio of the monoclinic zirconia to the tetragonal is 14:86. Neither a crystalline nor an amorphous silica was detected by XRD. This can be rationalized as follows: Silica exists as an amorphous phase, as will be described later, but the intensity of the diffuse peak of this phase is reduced by the high X-ray absorption of Zr.

The alumina–chromia coatings contained α-Al₂O₃–Cr₂O₃ solid solution as a major phase. The γ phase often observed in plasma-sprayed alumina ceramics was not detected in the present alumina–chromia coatings. A trace of an unknown phase (d = 2.06 Å) was observed in all of the alumina–chromia coatings.

3.2. Microstructures of Zircon Coatings
The plasma-sprayed zircon exhibits a some diversity of microstructures. Typical microstructures are shown in Fig. 2. The predominant structure, shown in Fig. 2(a), consists of fine grains of tetragonal ZrO₂ (≥200 Å) dispersed in SiO₂ glass. Particles of monoclinic ZrO₂ with a diameter larger than 0.1 μm are also dispersed in SiO₂ glass as shown in Fig. 2(b). Some parts reveal a duplex structure of the large monoclinic ZrO₂ with characteristic twins and the fine tetragonal ZrO₂ in SiO₂ glass as can be seen in Fig. 2(c). The EDX spectra in Figs. 2(d) and 2(e) were taken from the regions A and B marked in Fig. 2(c), respectively, with an electron probe of 0.05 μm in diameter. The EDX spectrum from region A indicates a slight amount of SiO₂ in ZrO₂ although the solubility of SiO₂ in ZrO₂ was negligibly small (less than 0.1% SiO₂). The EDX spectrum from region B indicates that fine ZrO₂ particles are dispersed in SiO₂ glass.

The microstructures similar to those shown in Fig. 2 were observed in plasma dissociated zircon (PDZ) crystals except for a large amount of SiO₂ glass retained in PDZ. The structure of PDZ was proposed to arise from the crystallization on supercooling due to rapid quenching as well as the segregation due to liquid–liquid immiscibility in ZrO₂–SiO₂ system. The cooling rate achieved in the present plasma spraying process is much higher than that in the plasma furnace for PDZ production. The micro-
structure of the plasma-sprayed zircon, therefore, can be understood to be formed solely by rapid cooling as will be mentioned in the following.

Solidification of isolated droplets initiates by homogeneous nucleation and undercooling down to approximately one-fifth of the equilibrium melting point. This can be applied to completely molten plasma sprayed particles and the solidification temperature is estimated approximately 1 900°C for ZrO\textsubscript{2} at the ZrSiO\textsubscript{4} content. The majority of zircon particles will completely melt and ZrO\textsubscript{2} will homogeneously nucleate from the liquid phase under extensive undercooling. Thus fine ZrO\textsubscript{2} particles, which are small enough to persist as the tetragonal structure, are dispersed in SiO\textsubscript{2} glass by the phase separation under rapid cooling. Some zircon particles partially melt to be molten SiO\textsubscript{2}-rich liquid and unmelted ZrO\textsubscript{2}. The unmelted ZrO\textsubscript{2} crystals may act as nuclei for subsequent crystal growth during cooling from liquidus temperature to approximately 1 900°C. Thus the large monoclinic ZrO\textsubscript{2} particles are thought to originate from the unmelted ZrO\textsubscript{2} crystals.

The plasma-sprayed zircon coatings are annealed at 1 300°C for 96 h in air. XRD analysis indicated that the coatings consist of a large amount of ZrSiO\textsubscript{4} and monoclinic ZrO\textsubscript{2} and a small amount of tetragonal ZrO\textsubscript{2}. The ratio of tetragonal ZrO\textsubscript{2} to monoclinic ZrO\textsubscript{2} changed from 86:14 in the as-sprayed coating to 7:93 in the annealed coating.

Some typical micrographs taken from the annealed specimen are shown in Fig. 3, although the annealed coating exhibits a diversity of microstructures. The dark and the bright regions in Figs. 3(a) to 3(c) reveal ZrO\textsubscript{2} and ZrSiO\textsubscript{4}, respectively. EDX spectra from ZrO\textsubscript{2} and ZrSiO\textsubscript{4} are illustrated in Figs. 3(d) and 3(e), respectively. The predominant structure in the as-sprayed coating, containing fine tetragonal ZrO\textsubscript{2} particles dispersed in SiO\textsubscript{2} glass, is thought to change into ZrSiO\textsubscript{4} during annealing. The residual ZrO\textsubscript{2} in the annealed specimen suggests a loss of SiO\textsubscript{2} from the original zircon. The loss must have taken place during spraying, since silica was reported to be vaporized extensively during the plasma-dissociation process. The microstructure similar to that in Fig. 3(c) was previously observed in the two phase ceramics of 25\%ZrO\textsubscript{2}-75\%ZrSiO\textsubscript{4} prepared by sintering of partially leached PDZ with 24 wt\% SiO\textsubscript{2}.\textsuperscript{10}

3.3. Microstructures of Alumina-Chromia Coatings

Al\textsubscript{2}O\textsubscript{3}-Cr\textsubscript{2}O\textsubscript{3} coatings plasma-sprayed with N\textsubscript{2} gas have two typical microstructures. One, which is observed predominantly in the as-sprayed coatings, reveals an equiaxed solidification structure of approximately 0.4 μm in grain size as can be seen in Fig. 4. Neither defects nor dislocations are observed in the grains. This feature is characteristic of rapidly solidified materials and has been observed in the plasma-sprayed Al\textsubscript{2}O\textsubscript{3}.

The other dominant structure in the coatings, shown in Fig. 5, is similar to a cellular solidification
both in the grain and at the grain boundary with an electron probe of 0.05 μm in diameter. The elemental analysis indicates that the precipitates along grain boundaries have a high Cr concentration.

The most probable phase for the precipitates is analyzed as a metallic Cr–Al solid solution among a lot of candidates of oxides or nitrides containing Cr and Al. If the precipitate is an oxide or a nitride, some other reflections having d-spacings larger than 2.06 Å should be observed in the electron diffraction pattern. The fact that only the reflection of d = 2.06 Å was observed from the precipitates indicates that this is not the case and that the precipitate is most likely a Cr–rich Cr–Al alloy which has a bcc unit cell; for instance Cr–12wt%Al solid solution has a = 2.928 Å. The strongest reflection of this phase is the 110 reflection having d = 2.07 Å. The Cr–Al alloy is thought to be formed by the reduction of Cr₂O₃ and Al₂O₃ during plasma-spraying process since the N₂ plasma-forming gas causes reducing atmosphere.

The above hypothesis for the formation of precipitates is supported by the observation of microstructures in the coatings sprayed by other plasma-forming gases which are more reducing than N₂ gas. Fig. 6 shows a typical example of the microstructure observed in the Al₂O₃–Cr₂O₃ coatings sprayed with an Ar–H₂ gas mixture. Many precipitates are observed along almost all the grain boundaries. The microstructure of the coatings in the N₂–H₂ gas mixture is
Fig. 5. Bright field (a) and dark field micrograph (b) taken with weak reflection arrowed in (c), showing precipitates along grain boundaries in Al₂O₃-Cr₂O₃ coating plasma sprayed with N₂ gas. Corresponding selected area diffraction pattern (c) indicating reflections from precipitates. EDX spectra (d) from regions in grain (indicated in white) and at grain boundary (black).

Fig. 6. Microstructure of Al₂O₃-Cr₂O₃ coating plasma-sprayed with Ar-H₂ gas mixture showing many precipitates along all the boundaries of polycrystalline Al₂O₃-Cr₂O₃ solid solution.

Fig. 7. Microstructures of the Al₂O₃-Cr₂O₃ coatings annealed at 1300°C for 96 h in air consist mostly of monoclinic ZrO₂ and ZrSiO₄. The residual ZrO₂ in the annealed coatings suggests a loss of SiO₂ from the original zircon materials during spraying. Large monoclinic ZrO₂ particles also dispersed in SiO₂glass. It is inferred that the fine tetragonal ZrO₂ particles originate from partially molten ZrSiO₄, which contains unmelted ZrO₂ crystals.

4. Conclusions

(1) The predominant microstructure of the plasma-sprayed ZrSiO₄ coatings is composed of fine tetragonal ZrO₂ particles dispersed in SiO₂ glass. Large monoclinic ZrO₂ particles also dispersed in SiO₂ glass. It is inferred that the fine tetragonal ZrO₂ particles homogeneously nucleate from the completely molten ZrSiO₄, while the large monoclinic ZrO₂ particles originate from partially molten ZrSiO₄ which contains unmelted ZrO₂ crystals.

(2) The ZrSiO₄ coatings annealed at 1300°C for 96 h in air consist mostly of monoclinic ZrO₂ and ZrSiO₄. The residual ZrO₂ in the annealed coatings suggests a loss of SiO₂ from the original zircon materials during spraying.

(3) Al₂O₃-Cr₂O₃ coatings plasma-sprayed with N₂ gas reveal the polycrystalline Al₂O₃-Cr₂O₃ solid solution with an equiaxed structure as the predominant microstructure. In some regions, fine precipitates presumably of Cr-rich Cr-Al alloy are observed along grain boundaries. Such precipitates appear at

not shown here but is essentially similar to that in Fig. 6. In a reducing atmosphere the reduction of Cr₂O₃ and Al₂O₃ results in the formation of precipitates of a Cr-rich Cr-Al alloy at grain boundaries. Such precipitates is likely to affect the wear resistance of the coatings since the Cr-rich Cr-Al alloy is inferior in wear resistance to the Al₂O₃-Cr₂O₃ ceramics. This is good agreement with the results of the wear test listed in Table 2.

Microstructures of the Al₂O₃-Cr₂O₃ coatings annealed at 1300 and 1600°C for 96 h in air are illustrated in Figs. 7(a) and 7(b), respectively. Both micrographs show the disappearance of precipitates characteristic in the as-sprayed microstructure and the extensive grain growth at higher temperatures. The precipitates may have dissolved or vaporized. Many pores at the dislocations in the grain as shown in Fig. 7(a) may be formed as a result of coalescence of vacancies induced by dissolution and/or volatilization of the precipitates during annealing. Dislocation loops such as shown in Fig. 7(c) are also thought to be formed as a result of coalescence of vacancies. The annealed coatings have microstructures similar to a sintered Al₂O₃-Cr₂O₃ material which includes a lot of dislocations both in grains and at low-angle grain boundaries as can be seen in Fig. 7(d).
almost all the boundaries in the coatings plasma-sprayed with N₂-H₂ or Ar-H₂ gas mixture. The precipitates are presumably formed as a result of reduction of Cr₂O₃ and Al₂O₃ during spraying.

(4) The precipitates along grain boundaries disappear during annealing at temperatures higher than 1300°C for 96 h in air.

(5) The wear resistance of Al₂O₃-Cr₂O₃ coatings is apparently affected by the precipitates.

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