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Preparation of Cross Sections of Thermal Spray Coatings for TEM Investigation

H. Zhang

A technique for the preparation of cross sections for transmission electron microscopy (TEM) of thermal spray coatings has been developed. The procedure is designed to minimize specimen damage during mechanical thinning and to reduce the effect of differential thinning during ion milling. Specimens were made by two different coating systems—WC-Co coating produced by the FARE Gun process on a mild steel substrate and Tribaloy T-800 sprayed by the HVOF process on a nickel-base superalloy. These specimens have large areas that are electron transparent on either side of the interface, and the results have shown the atomic scale microstructure of the interface between the thermal spray coating and the substrate.

1. Introduction

PRODUCTION of protective coatings for mechanical, thermal, and corrosion/oxidation applications has been the goal of surface engineering for many years. Thermal spray has become increasingly important as one of the most advanced coating technologies for modern industries.[1,2] The service performance of thermal spray coatings, like that of any other coating, is strongly related to the properties of the coating-substrate interface. Therefore, the study of microstructure, diffusion, phase distribution, and phase transformation in the interface region is of central importance to a fundamental understanding of the growth process and the failure mechanism of thermal spray coatings. Optical and scanning electron microscopy of coating cross sections have been the major tools used to examine the quality of the coatings. However, in most cases, bonding may exist in a region only a few nanometers wide (*i.e.*, 10^{-9} m or about 4×10^{-8} in.), which is far beyond the resolution of optical and scanning microscopes. Thus, transmission electron microscopy (TEM) becomes an ideal technique to carry out this kind of study. Such studies are important, because TEM offers not only higher resolution, but also thorough information about structure, defects, chemical compositions, and phase changes from very small areas, which could become the key to understand bonding mechanisms of the thermal spray coatings and to improved coating adhesion. However, due to difficulties in sample preparation, cross-sectional TEM for thermal spray coatings is not straightforward.

Techniques for preparing cross-sectional TEM specimen were first described by Abraham and Buiocchi [3] in the $GaAs_xP_{1-x}$/GaAs system and further developed by various research groups[4-7] in different systems, particularly involving semiconductor substrates. Cross-sectional TEM, including conventional and high-resolution TEM, has become one of the most important techniques to characterize semiconductor thin films and devices. Making a cross-sectional TEM specimen from thin films on engineering materials is more difficult. Nevertheless, Helmersson and Sundgren[8] have successfully imaged the interface region of a TiN thin film (4 μm thick) grown by reactive magnetron sputtering on a high-speed steel substrate. Unal *et al.*[9] have prepared cross sections of specimens for TEM studies of ZrO_2-$20Y_2O_3$ thin films made by electron beam physical vapor deposition (EB-PVD) on a nickel-base superalloy substrate. However, a reliable method for the preparation of cross sections of thermal spray coatings for TEM study has not been fully established. Because thermal spray coatings are formed under nonequilibrium conditions in an environment of air or a low vacuum,[1,2] the existence of internal stress, interfacial contamination, impurities, and inclusions cause the interface to be more sensitive to damage from mechanical handling, thus making the preparation of cross sections for TEM examination challenging.

Key Words: transmission electron microscopy (TEM), ion beam milling, tungsten carbide/cobalt coatings, microstructure, interface structure, chemical composition

H. Zhang, Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208 USA.

2. Experimental Methods

Two different coating systems—a WC-Co coating produced by the FARE Gun process on a mild steel substrate and Tribaloy T-800 sprayed by the High Velocity Oxygen Fuel (HVOF) process on a nickel-base superalloy—have been used. There are two

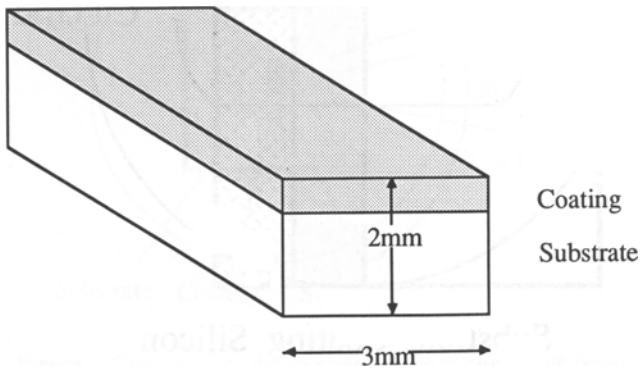

Figure 1 Cutting of slabs from a thermal sprayed sample.

main difficulties encountered during specimen preparation. The first is delamination of the coating layer from the substrate. Because of large differences in mechanical properties between the coating and the substrate, the interfacial bonding is usually not suitable for mechanical sectioning, and failure may occur during specimen preparation. The second is the development of a step at the interface during ion milling due to variable thinning rates for different materials. In most cases, the coatings have much lower thinning rates than those of the substrates, and thus the substrate may be entirely removed before the coating becomes sufficiently transparent to electrons. Therefore, for suitable sample preparation, it is essential to avoid debonding of the interface and to minimize differential thinning.

To accomplish specimen preparation, the material is sectioned into a 2 by 3 by 10-mm slab, as shown in Fig. 1, with a diamond saw or a wire cutting machine. Another slab (0.5 by 3 by 10 mm) cut from a material with a higher thinning rate during ion milling (like silicon, for example), is also prepared. Both slabs are then cleaned and degreased in acetone. After drying on a filter paper, the two slabs are cemented together with the coating layer in the center using M-Bond 610 Adhesive*, as shown in Fig. 2. The silicon slab protects the thermal spray coating from delamination during subsequent processing. The assembly is then held under mild pressure (similar to that exerted by finger pressure) in a vise and then cured at 100 to 150 °C for 2 to 4 hr, according to the manufacturer's instructions. For an as-sprayed coating, 80 °C for 10 hr can be used to avoid possible phase transformation. Furthermore, if the investigation is focused only on the interface structure, it is advisable to mechanically thin the coating layer to about 0.1 mm before sandwiching. After cooling, the specimen is removed from the vise and then sliced along a direction indicated by the dashed lines in Fig. 2, using either a diamond wafering saw or a wiring-cutting machine. The slice must be thick enough to avoid debonding during cutting. A reasonable thickness is 0.8 to 1 mm in most cases. If the cutting still fails, one may consider attaching a piece of silicon or metal to the specimen to either side perpendicular to the interface using mounting wax (Crystal-Bond) before slicing.

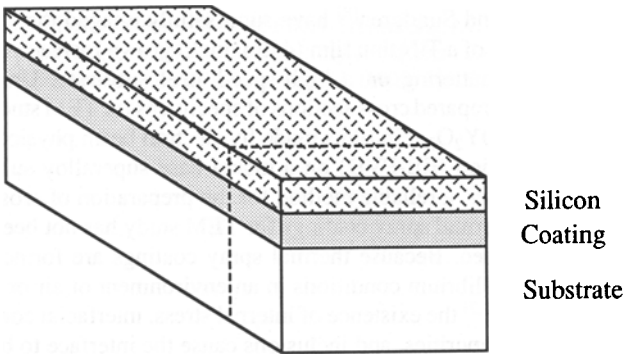

Figure 2 Silicon slab cemented to the coating. The dashed line indicates the position where a slice will be cut.

The specimen can now be mechanically thinned. A simple polishing tool, a stainless steel rod inserted into a cylindrical stainless steel holder, is necessary to keep the specimen surface flat and the thickness uniform. The specimen is mounted with wax onto the center of the stainless steel rod and then mechanically ground to about 200 μm using 600-grit paper. The grinding direction should be parallel to the interface to reduce chances of coating delamination, and the grinding should be done in flowing water to prevent the wax from overheating and melting. The sample is further polished with 800- and 1200-grit paper. Polishing with diamond paste on a soft cloth is not recommended because, although it produces a shiny surface, it may create a step along the interface. After this, the specimen surface is carefully

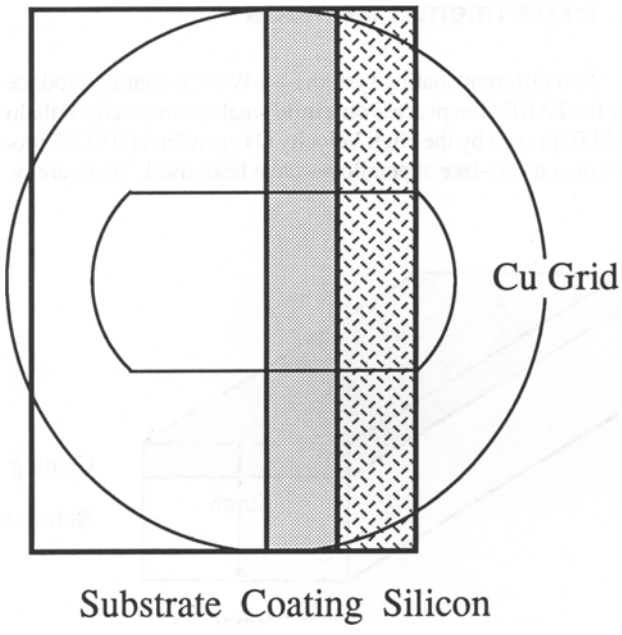

Figure 3 Orientation of the copper grid and specimen.

*M-Bond 610 is available from Measurements Group, Raleigh, North Carolina.

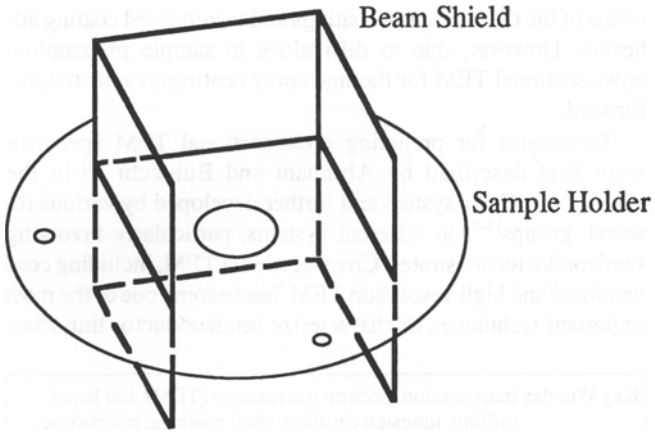

Figure 4 Platform used for ion milling. The beam shields mounted on both sides of the platform allow the ion beam to reach the specimen in 120° sectors.

cleaned with acetone using a soapy cotton tip to avoid any contamination from the mounting wax.

A TEM 2 by 1 slotted copper grid (3 mm in diameter with a 2-mm by 1-mm slot in the center) is then mounted to the specimen with M-Bond 610. The M-Bond is applied only to the copper grid, and the grid is placed in such a way that the interface is in the center of the slot and roughly perpendicular to the longer direction of the slot, as shown in Fig. 3. The advantage of this arrangement is that the ion beam hits the specimen from a direction perpendicular to the interface during ion milling. The specimen is then put into an oven for curing without being removed from the stainless steel bar. Immediately after taking the specimen out of the oven, a small piece of mounting wax is put on top of the specimen. The wax melts due to residual heat of the steel bar, and all bubbles in the wax can be removed by stirring the wax with tweezers. The specimen is then removed from the steel rod, turned over, and remounted on the steel bar with the copper grid facing down.

Once the wax is hard, the specimen is thinned to about 100 μm with 600-grit sandpaper and then dimpled from the same side (unpolished surface) using a dimpling machine. Again, care should be taken while mounting the specimen onto the dimpler stage to avoid bubbles beneath the specimen. By choosing a suitable load and rotational speed of the dimpler, the thickness in the center of the specimen can be reduced to about 20 μm. Further thinning is possible only on some more recent models of dimpling machines that have an accurate thickness controller. Before taking the specimen off the dimpler stage, any excess material hanging over the sides of the copper grid must be removed with a file. The dimpler stage is then placed on a hotplate. Once the wax holding the specimen has melted, the specimen is carefully pushed to the edge of the stage and picked up with tweezers. After cleaning in acetone to remove any residual mounting wax, the specimen is ready for ion milling.

If a dimpling machine is not available or if dimpling cannot be processed successfully, *i.e.*, debonding occurs during dimpling, then mechanical thinning using sandpaper can be continued. By carefully grinding with 600-, 800-, and 1200-grit sandpaper, 30- to 40-μm thick specimens of as-sprayed T-800 coatings have been obtained, which appear to be sufficiently good for ion milling. Measurement of thickness with an accuracy of ±5 μm is essential for this procedure. However, any measurement involving contact with the specimen may destroy it. Ideally, an optical microscope with focus control calibrated in microns is used. The measurement can be done by focusing the objective lens on the center of the specimen and the copper grid to which the specimen is attached, respectively, and the difference between the two readings provides the specimen thickness.

The final step of the procedure is ion milling. As mentioned before, traditional ion milling methods could not provide enough thin area in the interface region because of variation of the thinning rate between the substrate and the coating. To avoid this problem, a beam shield, made of three pieces of silicon (5 by 10 by 0.5 mm), is mounted onto either side of the platform of the sample holder using 5-min epoxy to block the ion beam. A 120° window is left for the ion beam to reach the specimen, as shown in Fig. 4. The specimen is placed in such a way that the coating faces the window, *i.e.*, incident beam, as shown in Fig. 5, so that the substrate near the interface is always under the shadow of the coating layer and thus locally achieves a thinning rate that is the same as that of the coating layer. The spacing between the silicon beam shields is not critical, but larger spacing does reduce contamination due to deposition of silicon on the sample. Silicon is used as the shield material, because any silicon that is deposited on the specimen surface can be easily removed with a low-angle ion beam (as detailed below), and thus contamination is kept to a minimum. The beam shields partially block the ion beam by two thirds, and therefore, the milling time will be three times longer than usual. A more efficient method is to mill the specimen in the traditional way (without beam shields) for a certain time and then transfer the specimen to the shielded platform for final thinning. Initial ion milling (without beam shields) usually takes less than 5 hr by using a Gatan dual ion mill operated at 5 to 6 kV with a 15° beam angle. The second stage of ion milling (with beam shields) commences when either the entire silicon slab is removed, or a small hole in the substrate or in the coating layer is formed. The second step of milling may take 1 to 3 hr. The beam angle may be reduced to 10 to 12° during the last half hour of thinning. It is important to watch the specimen closely once a hole has formed, and the thinning should be stopped as soon as the edge of the hold reaches the interface. The amorphous layer, which usually exists due to high-voltage ion milling, and the deposited silicon is removed from the specimen surface with a final stage milling at 3 kV and 10° without beam shields for 5 to 10 min.

3. Results and Discussion

The first TEM specimen was obtained from a WC-Co coating produced by the FARE Gun process on a mild steel substrate. Figure 6 shows the microstructure in the interface region. The coating layer appears to be uniform and contrast free, which is the typical characteristic of an amorphous phase. Diffused diffraction rings (inset figure on the top right corner) from this region confirm this speculation. Furthermore, Energy Dispersive

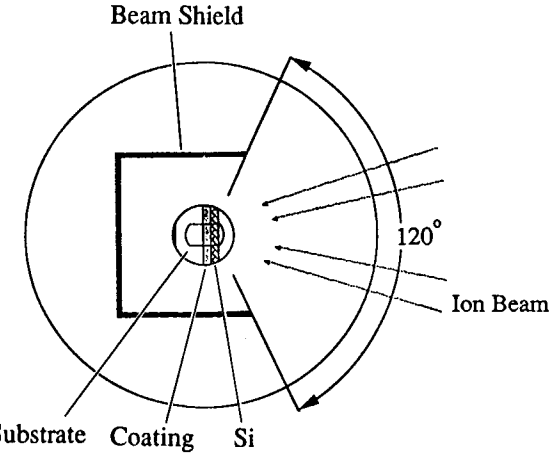

Figure 5 Orientation of the specimen in the platform with beam shields. The ion beam mills the specimen only from the 120° sector between the beam shields.

Spectrometry (EDS) analysis shows that this region exhibits the same composition as that of the material prior to spraying. The diffraction pattern from the substrate is in the lower left corner of the figure. Thus, these TEM observations indicate that melting or decomposition of WC crystals arises from the high kinetic energy of the WC particles, because the melting temperature of WC is much higher than the operating temperature of the FARE Gun process.

Figure 7 shows the interface region of Tribaloy T-800 sprayed by the HVOF process on a nickel-base superalloy. Diffraction from the coating layer shows uniform rings that are similar to the diffraction pattern from an amorphous phase, except that these rings seem too sharp to be characteristic of an amorphous material. The diffraction pattern from the substrate near the interface (inset figure on the lower left corner) appears as continuous sharp rings, which indicate the existence of very

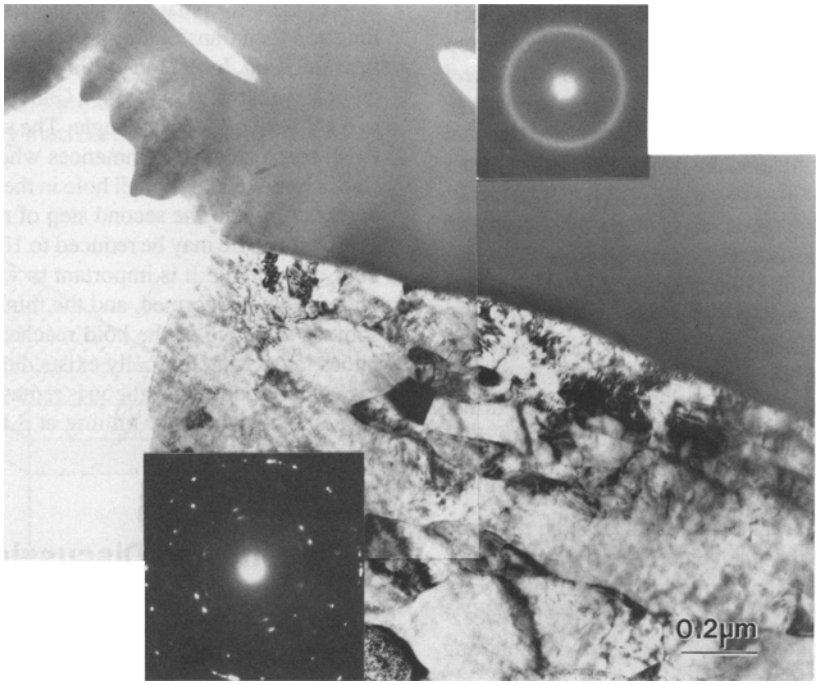

Figure 6 TEM micrograph shows the interface region of WC-Co coating produced by the FARE Gun process on mild steel substrate.

Figure 7 Interface region of Tribaloy T-800 sprayed by HVOF process on nickel-base superalloy substrate.

fine crystals in the region. Figure 8 is a high-resolution picture taken from the interface region, where lattice fringes and atomic images are directly exhibited. The figure is oriented so that the top of the coating is at the top of the page. It is observed that short-range ordering, or perhaps nano-scale crystals, exist in the coating region. A thin amorphous layer (about 2 nm), possibly formed due to interfacial contamination, exists between the coating and substrate.

Figure 9 shows the interface of the T-800 coating after heat treatment at 1050 °C for 5 min. The coating layer has entirely crystallized. Both the coating and the substrate have regularly shaped grains. Twins and stacking faults can be seen in the coating layer, whereas dislocations are observed in the substrate.

4. Concluding Remarks

A method of preparing cross sections of thermal spray coatings for TEM studies has been developed. Delamination of the coating during the thinning process can be avoided by applying a protective silicon layer on top of the coating, whereas homogeneous ion beam thinning is achieved by using beam shields. The same technique should be applied to any other coatings with weak bonding and large differences in thinning rates, such as metal, ceramic, and composite coatings. Examination of the bulk of the coating is also possible because a large, thin area across the entire coating layer has been formed during ion beam thinning.

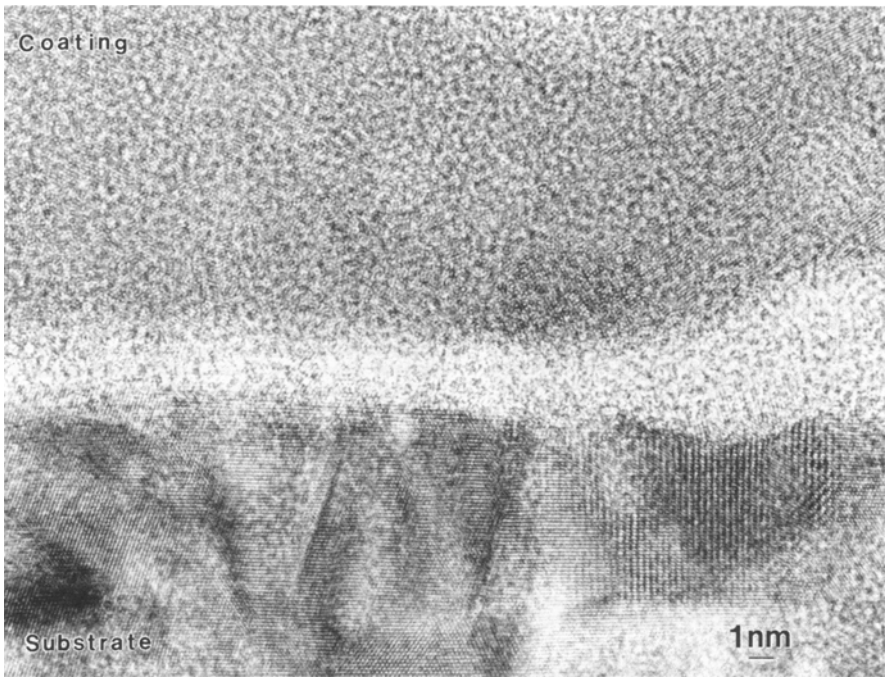

Figure 8 High-resolution image of interface region of as-sprayed T-800 on nickel-base superalloy.

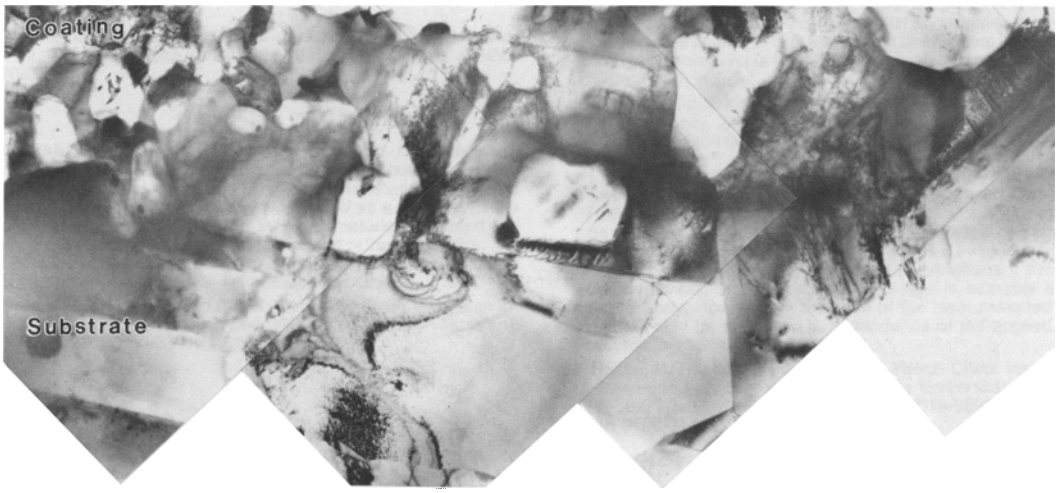

Figure 9 Microstructure of T-800 coating on nickel-base super-alloy after heat treatment.

The importance of examining cross-sectional specimens is not only to image the interface. By combining information on chemical composition (using EDS), electronic structure (using Electron Energy Loss Spectrometry, EELS), and high-resolution imaging, the interface can now be investigated in terms of fundamental interactions. It is possible to determine whether adhesion exists via metallurgical bonding, mechanical interlocking, or some other means. Furthermore, because specimens can be prepared as a matter of routine, the influence of thermal spray process variables can be examined in terms of substrate/coating interactions, which provides information on improving coating adhesion.

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