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The application of tripod polishing and focused ion beam milling to the TEM specimen preparation of HVOF thermally sprayed coatings

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ABSTRACT: The microstructure of high velocity oxy fuel thermally sprayed coatings is highly anisotropic and inhomogeneous. Tripod polishing has enabled the preparation of samples with up to 0.5mm diameter electron transparent areas, where a statistically significant number of features could be examined. Conversely, FIB has been used to prepare TEM samples for site-specific analysis of sub-micron regions of interest, e.g. for the interface characterisation between metallic coatings and the substrate, or the study of secondary precipitation on pre-existing phases in cermet coatings.

1. INTRODUCTION

High velocity oxy-fuel (HVOF) thermally sprayed coatings are produced by the successive deposition of individual splats from melted or partially melted powder feedstock. Because of the high particle temperatures and velocities involved in this process, and the high cooling rate on impact, HVOF coating structures are extremely heterogeneous [Smith, 1995]. TEM characterisation is required to fully understand the microstructure of such thermally sprayed coatings. However, the preparation of large area, electron transparent samples that truly represent the microstructural features of such coatings is quite a challenge for the traditional techniques of electropolishing or dimpling and broad ion beam milling, in addition to the investigation of site-specific features within the coatings. Accordingly, tripod polishing [Benedict, 1992] and focused ion beam (FIB) milling [Ishitani, 1991] have been applied to investigate HVOF thermally sprayed coatings. Representative results are presented enabling an appraisal of the advantages and disadvantages of each approach.

2. EXPERIMENTAL

An HVOF sprayed sample of composition Co-28Cr-4.5W-3.0Fe-3.0Ni-1.2Si-1.1C(wt%) is reported on here. TEM foils were first sequentially polished down to ~ 10μm thickness using a Testbourne Model 590W tripod polisher, then perforated using a Fischione 1010 low angle, argon ion beam thinning machine. An FEI FIB200 workstation was also used in this study for the examination of site-specific features within the HVOF coatings. Both

plan-view and cross-sectional TEM samples were prepared using the 'lift-out' technique [Hull, 1997]. An FEI XL30 FEG-SEM operated at 20 kV and a Jeol 2000fx TEM fitted with an energy dispersive X-ray (EDX) detector o perated at 200 kV were used to perform the microstructural characterisation.

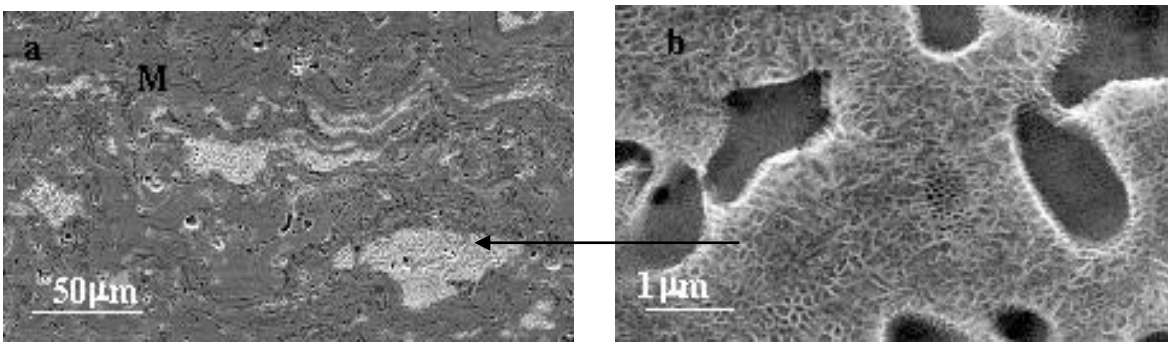

Fig. 1. SEM micrographs of an etched, HVOF sprayed Stellite 6 coating. (a) Cross-sectional image; (b) plan view image at higher magnification.

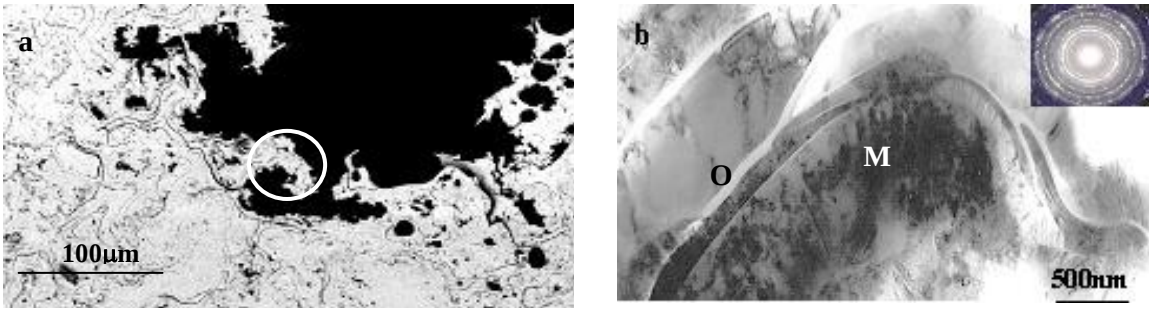

Fig. 2. (a) BSE image of TEM foil; (b) TEM image of circled region in 2a showing the layered structure of Stellite 6 coating with metallic matrix, M, and oxide layers, O. The inset SADP was taken from both the matrix and oxide.

3. RESULTS AND DISCUSSION

3.1 The application of tripod polishing and low angle argon ion milling

A Stellite 6 coating built up layer by layer onto a mild steel substrate with the formation of splats, intersplat oxides and some porosity is shown in the BSE image of Fig. 1a. The regions of lighter contrast that exhibit fine-scale dendritic features are attributed to powder particles that had not completely melted prior to impact on the substrate. Fig. 1b shows a higher magnification plan view micrograph of the area indicated in Fig. 1a. The rounded regions of darker contrast are the unmelted dendritic cores whilst the fine scale cellular structure is considered to have formed by the rapid solidification of the interdendritic liquid. Regions such as M (Fig. 1a) which appear relatively featureless in the SEM are believed to have formed from powder that was fully molten at the time of impact and then rapidly re-solidified at a high cooling rate.

The application of tripod polishing enabled TEM samples with ~ 0.5mm diameter electron transparent areas to be prepared and directly correlated with the features identified in SEM. Fig. 2a shows a low magnification BSE image of one particular TEM foil. The morphology of the circled region corresponds to the coating regime shown in Fig. 2b that had been fully melted, thereby, demonstrating the effectiveness of this sample preparation

approach. This TEM image shows several micrometer lengths of string-like oxide, denoted O, which partition the microcrystalline Co-based matrix regions, M. The oxide layers were 100 to 200nm in thickness and electron diffraction demonstrated them to be the spinel oxide $CoCr_2O_4$. The associated selected area diffraction pattern (SADP) corresponding to fcc Co and the spinel oxide is inset.

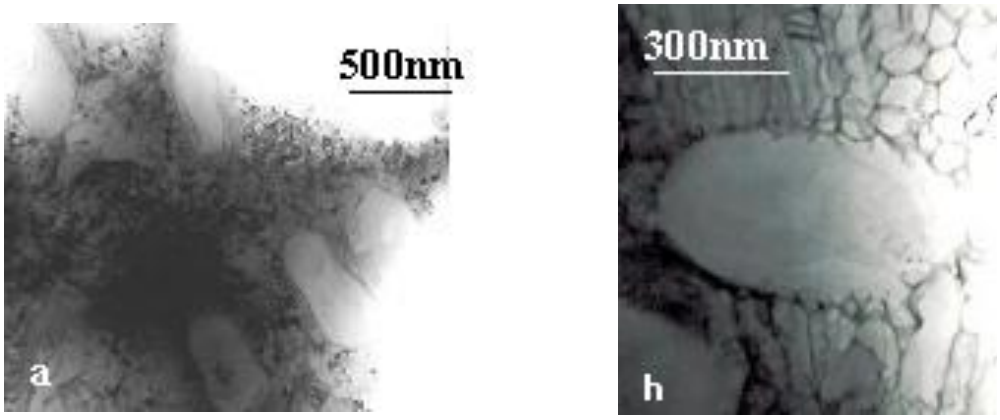

Fig. 3. (a) Bright field TEM image of a partially melted powder particle within the coating; (b) a high magnification image of a similar feature, showing remnant dendritic cores surrounded by a cellular structure.

Using the same approach, a partially melted powder particle within a coating was investigated, as illustrated by the low-magnification, plan-view image of Fig. 3a. The ~ 500nm-sized elliptical regions correspond to unmelted dendrite cores and these are surrounded by material exhibiting a cellular morphology (Fig. 3b). In this instance, the cell size of ~ 100nm is of a similar size to that revealed by SEM (Fig. 1b). EDX analysis indicated that the elliptical dendrite cores are ~ 15% richer in Co than the surrounding cell structure. It is considered that this compositional difference is the reason why these Co-rich dendrites were locally left unmelted during powder heating in the HVOF spray gun.

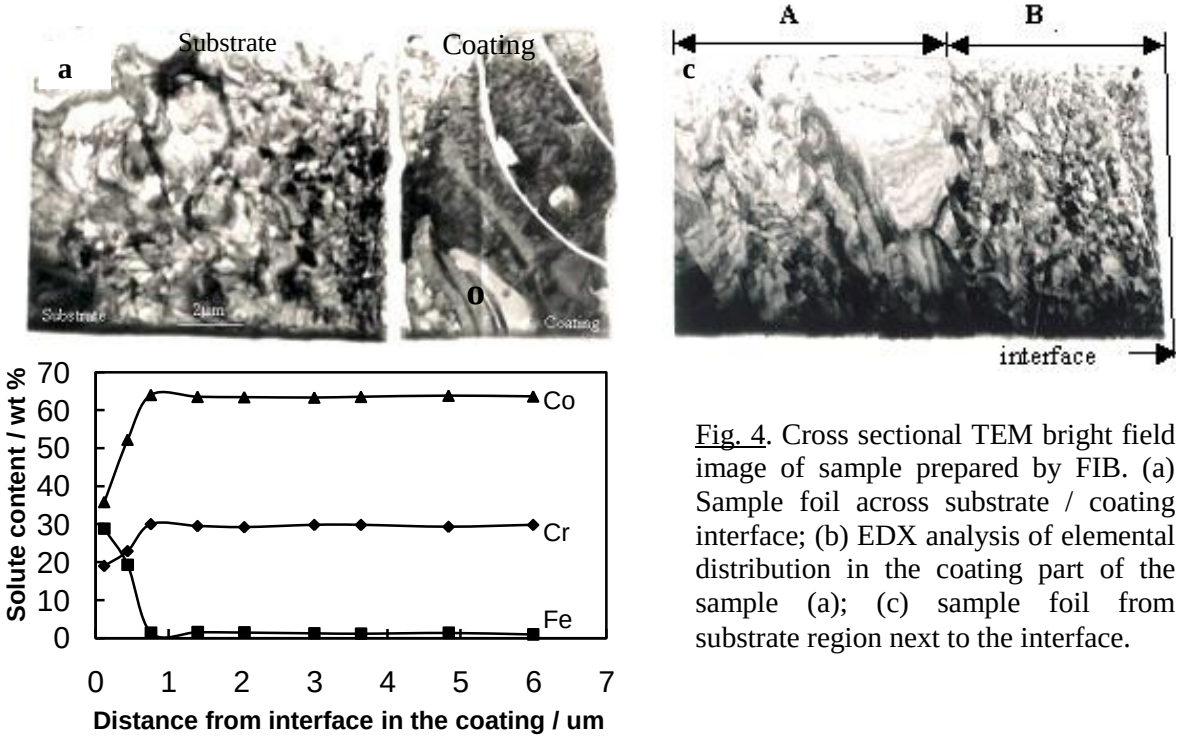

Fig. 4. Cross sectional TEM bright field image of sample prepared by FIB. (a) Sample foil across substrate / coating interface; (b) EDX analysis of elemental distribution in the coating part of the sample (a); (c) sample foil from substrate region next to the interface.

3.2 The application of FIB milling

An example of a cross-sectional Stellite 6 specimen prepared by the FIB "lift-out" technique is shown in the TEM image of Fig. 4a. Thin spinel oxide layers partitioning the fully-melted splats are identified within the coating, e.g. the feature labelled O. EDX analysis across the interface shows no trace of the coating elements within the substrate. However, a ~ 1 μm wide band of Fe was detected in the coating layer next to the interface (Fig. 4b). This suggests that very limited melting has occurred at the coating / substrate interface in this instance. At the moment a molten / semimolten coating powder impacts on the mild steel substrate, a limited amount of Fe will dissolve into the coating material. However, it is considered that the impact momentum and temperature of the coating particles is insufficient to fully melt the substrate which remains solid. Accordingly, no coating species is able to diffuse into the surface of the substrate. It is also interesting to note how the microstructure of this mild steel substrate gradually changes with distance from the interface deeper into the substrate. This phenomenon is more clearly illustrated by Fig. 4c which shows a TEM membrane cut from a region of the mild steel substrate close to the interface. It shows a highly deformed band A and a recrystallisation band B as a consequence of thermal spikes associated with the spray deposition process. Because a grit blasting surface roughening treatment was applied to the substrate before thermal spraying, a certain amount of deformation was built up in the top surface layer. During the subsequent process of thermal spray coating, it is believed that the temperature at the interface is sufficient to induce recrystallisation recovery within this deformed substrate layer, hence the microstructural change observed in the substrate. As limited melting occurred between the substrate and coating, the bonding between them is considered to be dominated by mechanical coupling.

Tripod polishing is undoubtedly the preferred choice for the general microstructural mapping of HVOF coatings because of the large size of electron transparent areas produced. The ability to minimise artefacts and surface amorphisation damage also make this the preferred route for preparing samples requiring chemical microanalysis. However, these advantages are sometimes offset by the problem of preferential argon ion milling of a multi-phase coatings. Conversely, the ability to perform site-specific analysis of a coating / substrate interface, or an interphase reaction within these thermally sprayed coatings, by the FIB approach clearly offers an advantage. However, it is noted that there is always some degree of remnant amorphisation at the two side-walls of these FIB prepared sample foils, the thickness of which is dependent on the material and the milling parameters.

Acknowledgements

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References

Smith R. W, Knight R, *JOM*, 47 (1995) 32.
Benedict J. P, Anderson R. M, and Klepeis S. J, Mat. Res.Soc. Sypm. Proc. 254 (1992) 121.
Ishitani T, Ohnishi T, Madakoro Y, Kawanami Y, *J. Vacuum. Sci. Technol.* **B9** (1991) 2633.
Hull R, Banck D, Stevie F. A, Koszi L. A, Chu S. N. G, *Appl. Phys. Lett.* **62** (1997) 3408.