Effect of Manganese on the Microstructure of Cemented Carbides

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Abstract

The plastic deformation behavior of cemented carbides is related to the WC grain boundary strength. Ab initio calculations predict that Co and Mn segregate to WC/WC grain boundaries. To experimentally study the effect of Mn, a WC-Co-Mn material was manufactured and compared to a WC-Co material. The microstructure was studied using scanning electron microscopy (SEM), including electron backscatter diffraction (EBSD). Special attention was paid to the WC grain size and the frequency of special low-energy grain boundaries. Mn was found to have negligible effect on both the WC grain growth and the fraction of $\Sigma 2$ WC/WC boundaries in the as-sintered material.

Keywords : WC-Co, Mn, EBSD, grain boundary segregation

1. Introduction

The plastic deformation behavior of cemented carbides during operation is related to the WC grain boundary strength. Recent *ab initio* calculations by Christensen and Wahnström¹ predict that Co and Mn will segregate to WC/WC grain boundaries. These calculations also suggest that the presence of Co and Mn at WC/WC interfaces increases their work of separation, hence strengthening the grain boundaries. It has been experimentally verified that Co segregates to the WC/WC grain boundaries².

To investigate these predictions, Mn was added to a cemented carbide alloy.

2. Experimental and Results

The WC-Co-Mn was produced using conventional powder metallurgical routes. This includes mixing by milling for 8 h, drying, compaction and sintering. The sintering was performed at 1410 °C for 1 h in vacuum. As Mn-source pure Mn powder was used (Koch-Light Lab Ltd. Mn powder 99.9w%). Special precautions were taken to minimize the amount of sulphur to prevent the formation of MnS. The chemical composition of the materials is given in Table 1 and the physical properties of the materials are given in Table 2. The microstructure of the materials is shown in Figs. 1 and 2.

To study the impact of Mn on the WC grain size EBSD was used. The EBSD system was also used to measure the fraction of low energy $\Sigma 2$ WC/WC boundaries in the materials (Table 3). The $\Sigma 2$ WC/WC boundaries exist where

Table 1. Chemical analysis of the as-sintered Mn material and reference in mass%.

Compositions	W*	С	Со	Mn
WC-Co-Mn	84.26	5.44	9.90	0.17
WC-Co	84.80	5.41	9.89	0.00

* W by difference

 Table 2. As-sintered properties of Mn material and reference.

	HC*	S**	Dens.	Porosity	HV3
	(kA/m)		(g/cm^3)	(ISO4505)	
WC-Co-Mn	13.2	0.87	14.55	A01B00	1390
				C00	
WC-Co	14.1	0.87	14.58	A00B00	1397
				C00	

* Coercivity ** Relative magnetic saturation to Co (by weight)

the grains have a rotation of 90 degrees about the [10-10] axis. Brandon's criterion³ is used for level of acceptance of deviation from the CSL; *i.e.* 10.6 degrees. The results of the EBSD investigations are given in Table 3.

In order to detect any Mn segregation to WC/WC grain boundaries, a transmission electron microscopy (TEM) specimen was produced. The specimen was studied using a Philips CM200 FEG-TEM equipped with a Link Isis energy-dispersive X-ray spectrometry (EDS) system. Four WC/WC grain boundaries were investigated with EDS. No Mn was detected. The result from a typical boundary is shown in Fig. 3. The non-zero signal from the Co in the WC is a specimen preparation artifact.



Fig. 1. SEM image of the WC-Co-Mn material.



Fig. 2. SEM image of the WC-Co material.

Table 3. Grain size measurements from EBSD (equivalent circle diameter) and fraction of $\Sigma 2$ WC/WC boundaries (length of $\Sigma 2$ boundaries / total high angle boundary length).

	Mean grain	Std dev. of	Fraction of
	size (µm)	grain size	$\Sigma 2 WC/WC$
		distribution	boundaries
WC-Co-Mn	0.69	0.41	0.177
WC-Co	0.71	0.41	0.175

Two grain boundaries in the Mn material were analyzed with an energy compensated tomographic atom probe (EcoTAP) produced by CAMECA. Both grain boundaries contained approximately half a monolayer of Co. No Mn atoms could be detected. The reconstruction of one of these analyses is shown in Fig. 4.



Fig. 3. EDS analysis across a WC/WC grain boundary.



Fig. 4. EcoTAP analysis of WC-Co-Mn material. Co atoms are magnified.

3. Summary and conclusions

According to the present investigation Mn was found to have negligible effects on the WC grain growth and the fraction of $\Sigma 2$ WC/WC boundaries in the as-sintered material by means of EBSD. However, there is a difference in the coercivity value. The reason for this needs further investigations.

In the manufactured material, no Mn was detected at the WC/WC grain boundaries by means of TEM/EDS and atom probe.

4. References

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