Int. Journal of Refractory Metals and Hard Materials 49 (2015) 57–66

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

The role of tungsten in the Co binder: Effects on WC grain size and hcp–fcc Co in the binder phase

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ARTICLE INFO

Article history:
Received 2 March 2014
Received in revised form 27 August 2014
Accepted 26 September 2014
Available online 30 September 2014

Keywords:
Binder phase composition
WC grain size
Binder phase structure

ABSTRACT

Recent advances in microscopy techniques have made possible the quantitative examination of the Co binder phase in WC–Co cemented carbides [1]. The composition of the binder phase is of interest with respect to applications where fracture toughness and fatigue are particularly important. A previous work has observed that the hcp/fcc ratio can change with fatigue and applied stress [2].

This work is part of a wider study examining the role of Co mean free path, mean WC grain diameter (d_{WC}) and composition on the hcp–fcc content on the Co binder phase extracted from a wide range of WC–Co samples with an average d_{WC} of 0.6 μm < d_{WC} < 10 μm and Co content from 6 wt.% to 25 wt.%. This paper aims to study the effect of carbon composition on three 10 wt.% Co grades with target d_{WC} 0.8 μm < d_{WC} < 6 μm. The concentration of W in the Co was monitored by examining the binder magnetic saturation (BMS). Samples with a variety of Co M_{sat} values through the WC–Co pseudo-binary phase field were studied. The effects on grain size, Co distribution, physical properties and hcp content with varying W content were examined. Experimental results show that lower BMS resulting from dissolved tungsten in the binder has a negative exponential correlation with hcp abundance for grades with d_{WC} < 1.5 μm. A significant abundance of hcp was associated with a more diffuse large scale fcc–fcc structure of the binder phase, which has been associated with improved crack deflection [14].

This work belongs to the Special Issue of the International Conference on the Science of Hard Materials (ICSHM10).

1. Introduction

Cemented carbides have a wide range of demanding applications in which toughness and fatigue resistance are critical. These properties are controlled by the ductile binder phase component of the cemented carbide. Co is the usual choice of binder for cemented carbides due to its excellent wetting properties at sintering temperature, enabling infiltration of the carbide skeleton, and production of fully dense cemented carbide tools in a wide variety of grain sizes and geometries. Thermal expansion mismatch between WC and Co means that the WC is in compressive stress, and with Co is in tension that further increases the strength of the carbide–binder composite[0].

W is soluble in pure Co up to 8.0 at.% [3,4] which hardens the Co binder phase via solid-solution strengthening, and aids full densification during sintering in cemented carbide. For the pseudo-binary WC–Co system with a Co content set at 10 wt.%, the stable two-phase region corresponds to a total carbon content of between 5.4 and 5.55 at.% [3]. Using the depression of Co equivalent magnetic saturation [4,5], which can be defined as the Binder Magnetic Saturation (BMS) it is possible to calculate the concentration of tungsten in the binder phase. In this work, BMS is expressed as a percentage of the magnetic saturation of pure Co at room temperature, which is taken as being equivalent to 2.029×10^{-4} T m [3,4]. Therefore, a quantitative relationship between Co M_{sat} (BMS) and W at.% concentration can be determined as defined by Eq. (1):

$$\sigma - \sigma_0 = -8\, m_w \times 10^{-7}, \tag{1}$$

where σ_0 is the magnetic saturation of pure Co in Tesla (T m^3); σ is the measured magnetic saturation of the material being tested in Tesla (T m^3); m_W is the atomic % of tungsten dissolved in the binder phase. From this formula, it is possible to calculate m_W:

$$m_w(\text{wt.\%}) = \frac{(M_{Sat} - M_{Co})}{-8 \times 10^{-7}}. \tag{2}$$

From Eqs. (1) and (2) the upper and lower limits of the pseudo-binary WC–Co phase field are equivalent to BMS values of 85% and 95% respectively. When considering the concentration of W in the binder phase, this is equivalent to a W abundance of around 4 at.% at the lower limit, defined where M_6C η-phase is present and 1 at.% at the

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http://dx.doi.org/10.1016/j.ijrmhm.2014.09.028
0263-4368/

graphite limit. The effects of unwanted ternary phases on hardness, toughness and wear resistance are well known, but there has been less focus on the effect of variable carbon balance within the two-phase region. The aim of this work is to establish how different carbon contents affect the structure and properties of WC–Co carbides, and the implications for current quality control and tool applications. Of particular interest is the impact of carbon balance on the hcp–fcc content of the Co binder phase, and the implications for fatigue resistance and crack deflection.

The quantity of dissolved W present in the Co binder observed has a significant impact on the hcp–fcc phase distribution [4]. Previous experiments with dilute Co–W–C alloys simulating the Co binder phase [4] observed that alloys with W greater than 5.9 at.% were exclusively fcc Co with a corresponding depressed BMS. Ductility and Co grain size were observed to increase with greater fcc concentration for the as-cast alloys, which has implications for how binder phase chemistry affects the overall properties of a hard material composite. Similarly, there is little data on the low temperature WC–Co phase diagram as the majority of research into phase diagrams considers systems at temperatures greater than 800 °C [3]. There is a possibility that two samples of the same initial Co wt.% and target sintered d_{WC} carbide powder with BMS values at different ends of the pseudo-binary limit, could have sufficiently different hardness, toughness and sintered d_{WC} that they could qualify as different materials.

A previous work examining variables affecting the hcp–fcc content of cemented carbides have focused on grain size and Co content [6,7]. While a statistically significant correlation ($p = 0.0454$) between grain size and hcp content was observed, the R^2 factor of 0.45 showed a high degree of scatter consistent with a range of BMS values within the WC–Co phase field. No significant correlation was observed for Co mean free path (λ_{Co}) and hcp content and the low value of R^2 is indicative of the sensitivity of hcp content to W content. The main criterion for samples prepared in these studies [1,6,7] was to be within the two-phase region irrespective of Co M_{sat} values. This study aims to redress the limitations of previous studies examining the variables affecting hcp content in binder phase by generating a series of samples within the pseudo-binary WC–Co region for three different 10 wt.% Co grades with target WC grain sizes of 0.8 μm, 2 μm and 6 μm respectively.

2. Method

Samples were made from carbide powder with target sintered grain sizes of 0.8 μm (Grade A), 2.0 μm (Grade C) and 6.0 μm (Grade E), respectively. All samples had Co at 10 wt.% as the binder phase with C and W additions to adjust the carbon balance. Powder batches were made up with incremental C or W additions to produce a selection of samples with varying BMS from the η-phase to graphite limits of the pseudo-binary WC–Co carbon window. C and W additions were calculated for each grade depending on the initial BMS of a sintered sample with no additions. BMS values from unmodified carbide powder were 79.9%, 87% and 94.9% for grades A, C and E, respectively. Total carbon mass% for WC powder as received was found to be 6.11%, 6.15% and 6.18% for grades A, C and E. 6.13 mass % C is the value for stoichiometric WC.

Samples were made using conventional laboratory based powder metallurgy methods. Powders were initially mixed in 100 g batches in 0.25 l carbide lined mills using WC and Co metal powders in the appropriate ratio. An organic binder was added at 2 g/100 g powder charge as a pressing agent along with 50 ml of ethanol. Milling media was added at a media: powder charge ratio of 12:1 for grades A and C and 9:1 for grade C. Measurements for bulk powder with a Sartorus balance were accurate to 0.01 g; C and W additions were made using a Mettler A30 balance accurate to ±0.0001 g. Milling times were 8 h for grades A and C and 2 h for grade E. Additions of C and W were made by placing 25 g of blended powder with C or W additions in a 125 ml Perspex container with 25 ml ethanol and blended by high-energy mixing at 60 Hz for 30 min to produce a slurry prior to drying and pressing. Sintered samples were labeled based on their target sintered grain size and their measured BMS. Sample names along with C and W additions for each series of samples are given in Table 1.

Powder was pressed then sintered in a vacuum furnace with a 1 h dwell at 1410 °C. Average sintered dimensions of test pieces were 20 mm × 6 mm × 5 mm with a mean mass loss of 2%. Shrinkage was observed to vary from 18%–19% with the sample having the lowest BMS and having the greatest shrinkage during sintering. The magnetic moment (BMS) was measured using a Setaram magnetometer with an uncertainty of 0.2%, providing there is a consistent sample geometry. Coercive field H_c was measured using a Foerster Koerzimat with an uncertainty of 0.01 kA m^{-1}. Density was measured using the Archimedes method using a Mettler Toledo precision balance with an uncertainty of ±0.001 g at 20 °C. Hardness was evaluated using a Vickers diamond 30 kg load (HV30) using no less than 5 indents per sample with a measurement error of ±5% for all grades. Palmqvist cracks were used to evaluate toughness via the critical stress intensity factor $K1_c$ using the Shetty method to calculate $K1_c$. HV100 loading was used to generate cracks for the 10 E series.

Microstructure was characterized using the ISO 4505 procedures for assessing porosity, ternary phases and abnormal grain growth on polished sample cross-sections. Samples did not have significant porosity from sintering. Some samples at the WC–Co limits did have trace ternary phase presence and are indicated in Table 1. Data on the physical properties of sintered samples is shown in Table 2 in the Results section. Images of microstructure from samples at either end of the WC–Co phase field are shown in Fig. 1.

Samples with a more W-rich Co binder generally had more prominent Co lakes and rounder WC grains than those with a higher carbon activity.

2.1. WC grain size measurement

Tungsten carbide grain size was evaluated using Electron Back Scatter Diffraction (EBSD). Two methods were used to evaluate carbide grain size (1) volume median derived from the equivalent circular diameter [6,7] and (2) mean diameter via 2D polygonal fitting using a graphical tablet and grain size measurement software (Analysis Auto™) [6]. The WC grain diameter d_{WC} is defined as the longest possible linear diameter fitting within the 2D polygon. Similarly, the Co mean free path λ_{Co} is also defined in terms of the longest linear diameter within the 2D polygon fitted to a Co ligament. In this work, a Co ligament is any interstitial region between adjacent WC grains in which Co is present. Comparing different methods used for evaluating grain size in cemented carbides [6–8] has shown that the linear intercept method gives the best fit when correlating d_{WC} against HV30 and H_c but the difference in the R^2 values between 2D polygonal ($R^2 = 0.91$) fitting and the linear intercept method ($R^2 = 0.93$) is not significant. 2D polygonal fitting has additional advantages in that it can be used to directly measure the Co mean free path λ_{Co}. The polygonal fitting method can be used both with EBSD generated orientation image maps (OIM) and with standard optical or

Table 1
Sample composition and nomenclature.

Grade A 0.8 μm	Additions g	Grade C 2 μm	Additions g	Grade E 6 μm	Additions g
10A 79	0	10C 74	0.6 W	10E 77	0.6 W
10A 82	0.001 C	10C 79	0.3 W	10E 89	0.3 W
10A 87	0.002 C	10C 87	0	10E 92	0.2 W
10A 91	0.003 C	10C 91	0.001 C	10E 94	0
10A 93	0.004 C	10C 93	0.002 C	10E 96	0.001 C
10A 97	0.005 C	–	–	–	–

Additions per 25 g powder charge.