Variation of WC grain shape with carbon content in the WC–Co alloys during liquid-phase sintering

Sona Kim a, Seok-Hee Han b, Jong-Ku Park b,*, Hyoun-Ee Kim a

a Center for Microstructure Science of Materials, School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Republic of Korea

b Nano-Materials Research Center, Division of Materials, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

Received 25 February 2002; accepted 10 September 2002

Abstract

WC–Co hard metals have faceted WC grains dispersed in a ductile cobalt-rich matrix. The effect of carbon (C) content on the shape of WC grain in the WC–Co metals during liquid-phase sintering is investigated in this work. The WC grain shape varies with the C content and, more importantly, the shape change occurs reversibly with the C content.

© 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Sintering; Carbides; Carbon content; Microstructure; Grain shape

1. Introduction

Cemented tungsten carbides with cobalt binder (called WC–Co hard metals), which has wide applications as a wear-resistant tool material, are usually fabricated by using liquid-phase sintering. In the WC–Co metals, faceted WC grains are dispersed in the cobalt matrix [1–3] and grow through Ostwald ripening during sintering [4]. It has been observed that the WC grains in WC–Co alloys have a truncated trigonal prism shape regardless of the alloy composition [5–7]. It was observed that various phases exist in WC–Co alloy and their phase boundaries are sensitively affected by both Co and C contents [8]. Given the strong effect of the carbon (C) content on various characteristics of WC–Co alloys, there is a possibility that the WC grains change their shape with the C content [8–11] and this possibility is explored in this work; namely, the WC grain shape is examined with varying the C content of WC–Co alloys during liquid-phase sintering.

2. Experimental procedure

The following powders were used in the present study: WC (1.24 μm, 99.99%) produced by Tae-guTec (formerly Korea Tungsten Mining Co.) and Co (2.4 μm, 99.9%) and C (lump-black carbon) supplied, respectively, by Hermann C. Stark and Fisher Scientific Company. The powders were weighed separately according to the predetermined ratio and then mixed mechanically. The powder....
mixture was milled for 72 h, dried in a vacuum oven and then granulated for easy and homogeneous compaction. A special care was taken to avoid possible compositional contamination during milling by using a jar lined with a pure WC–Co alloy, together with balls of pure WC–Co.

Two different alloys, WC–30%Co and WC–35%Co, were chosen as fundamental compositions and the amount of carbon added to the alloys was varied from 0.1% to 1.5%. Note that all the compositions are in weight percentage. The granulated powders were compacted into cylindrical disks with a diameter of 10 mm at a pressure of 25 MPa. The compacts were sintered in vacuum at 1450 or 1500 °C in a furnace with a graphite heater. In a separate model experiment, some sintered compacts were imbedded in a pack of carbon black powder and sintered again in order to provide the carbon to the interior of the presintered compacts.

The sintered specimens were cut and polished for microstructural observation by optical microscopy. For a clear observation of WC grain shape by scanning electron microscopy, WC grains in the sintered compacts were extracted by removing the cobalt-rich matrix with a boiling 20% hydrochloric solution.

3. Results and discussion

The WC–30%Co alloy sintered at 1450 °C for 2 h exhibited various microstructures depending on the C content (Fig. 1). Each microstructure belongs, respectively, to a three-phase region consisting of WC, β-Co and η phases (Fig. 1(a)), a two-phase region consisting of WC and β-Co (Fig. 2(b)), and a three-phase region consisting of WC, β-Co and free carbon (Fig. 1(c) and (d)) [12]. Here, the β-Co phase is a cobalt-rich solid solution containing W and C, which is a liquid phase at the sintering temperature and the η phase is Co3W3C, usually found in the WC–Co alloy with an insufficient C content. Large WC grains (hereafter simply called the large grains) are randomly dispersed in the fine grain matrix. The large grains in these alloys show similar shapes. With the increase of C content from 0.1% C to 1.0% C, the WC grains tend to show an elongated rectangular shape. This means that the WC grains grow preferentially along the [100] crystal direction together with increase in the C content of WC–Co alloys. In addition, the large grains follow the general tendency of accelerated growth of WC grains in the compacts of high C content [8].

Fig. 1. The microstructure of WC–30%Co alloys with varying C contents of (a) 0.1%, (b) 0.3%, (c) 0.7%, and (d) 1.0%. All the compacts were sintered together at 1450 °C for 2 h.
Fig. 2 shows the WC grains extracted from the WC–30%Co alloys sintered at 1450 °C for 8 h. It is evident that, at C contents above 0.7%, the large grains with the nearly triangular prism shape begin to appear. Fig. 2(a) shows that faceted steps on the basal plane of WC grains become prevalent in the 0.1% C compacts with low C content. However, this evolution of stepped basal planes in the growing WC grains remains unexplained. Additionally, the WC grains in the 1.0% C compact with high C content (Fig. 2(d)) look a little smaller than those in the compacts with less C content. This small grain size in the compact of high C content is attributed to the free carbon particles existing in the three-phase region, which hinder the WC grains from growing by mechanically suppressing the motion of WC grains in the Co-rich liquid [15].

Fig. 3 shows the results obtained from the model experiments. The large grains extracted from the WC–35%Co–0.7%C alloy sintered at 1500 °C for 2 h exhibit a truncated trigonal prism shape (Fig. 3(a)). When the same compact is imbedded in the carbon powder pack and sintered again for 5 h at the same temperature, the WC grains result in a triangular prism shape (Fig. 3(b)). The results in Fig. 3 are direct evidence showing the reversible change of WC grain shape with the C content. The
present observation is quite different from the general acceptance of invariable WC grain shape. Therefore, the well known truncated trigonal prism shape of WC grains in the WC–Co alloys is not an equilibrium shape, but a growth shape determined kinetically at a given C content of the alloys.

The shape change of WC grains in Fig. 3 is only possible when one of the two families of prismatic planes grow preferentially and/or more rapidly along the [100] directions along with increase in the C content of the alloys. This difference in growth kinetics among the prismatic planes in a same WC grain seems to be closely related with the atomic structure of WC crystal. WC crystal has a \( P_{6}m2 \) crystal symmetry [13,14]. The carbon atoms take the asymmetric position of \((1/3, 2/3, 1/2)\) in the unit cell as shown in Fig. 4 and this asymmetric occupation of carbon atoms divides the prismatic planes into two different families of planes with different atom arrangements. These two families of prismatic planes can have a different affinity to carbon because W atoms on each plane have a different number of W–C bonds. The planes with high affinity to carbon grow preferentially in the saturated carbon conditions and disappear finally leaving triangular prism in shape. Practically, from a simple calculation based on broken bond model [16], it is confirmed that a family of prismatic planes in a WC crystal has surface energy quite different from the other. However, each crystallographic plane in the WC crystal cannot be assigned to the corresponding plane in the real WC grain. Also the appearance of new planes indicated by the arrows in Fig. 2(b) can be explained also by the atomic structure of WC crystal. The angle measured between two new intersecting planes is 97.06°, which agrees well with the calculated angle between the planes of \((10\overline{1}1)\) and \((10\overline{1}1)\). These new planes possess the highest density of W and C atoms in the WC crystal.

4. Conclusions

It was observed for the first time that the WC grains in the WC–Co material exhibit various shapes and change their shape reversibly as the C content varies. The triangular prism shape of WC grains was shown to be an equilibrium shape observed only in the WC–Co alloys with the saturated C content. The various shapes of WC grains from truncated trigonal prism to triangular prism are growth morphologies kinetically determined depending on the C content. The dependence of WC grain shape on the C content is attributed to an asymmetric occupation of carbon atoms in the crystal structure of WC. Additionally, the asymmetrically occupied carbon atoms were considered to be responsible for the appearance of new crystallographic planes of \(\{10\overline{1}1\}\) type.

Acknowledgements

The work was partly supported by the program of National Research Laboratory funded by the Korean Ministry of Science and Technology.

References


