Int. Journal of Refractory Metals and Hard Materials 52 (2015) 245–251

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

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

Carbon content dependence of grain growth mode in VC-doped WC–Co hardmetals

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ARTICLE INFO

Article history:
Received 9 April 2015
Received in revised form 27 June 2015
Accepted 2 July 2015
Available online 7 July 2015

Keywords:
Hardmetals
Cermets
TEM
EDS
Grain growth
Liquid phase sintering

ABSTRACT

Carbon content dependency of grain growth mechanism and grain growth inhibition mechanism in VC-doped WC–Co hardmetals is investigated. VC-doped WC–Co hardmetals with three different carbon contents were sintered with liquid phase and then rapidly quenched to freeze up the structure at the sintering temperature. In these samples, spatial distributions and atomic scale structures of V-rich phases are investigated using transmission electron microscopy (TEM) and related techniques. In these measurements, doped V is found in liquid phase as solute, in large $(W,V)C_x$ precipitates and in interface segregations. Further detailed observations and discussions are carried out for the $(W,V)C_x$ segregated at the WC grain/Co phase interfaces. These $(W,V)C_x$ phases change their form from planar films to small islands depending on the carbon content. The WC grain/Co phase interfaces are fully covered by planar $(W,V)C_x$ in the sample of low carbon content. On the other hand, the WC grain/Co phase interfaces are partially covered by $(W,V)C_x$ islands in the material of high carbon content. During sintering, the WC grains in this sample grew much faster than those in the sample of low carbon content. These structural differences are discussed in terms of WC grain/$(W,V)C_x$ interface energy.

1. Introduction

WC–Co based hardmetals are widely used as bits for cutting, mining and many other machining tools because of their remarkable hardness and wear resistance [1,2]. They are commonly prepared by liquid phase sintering at the temperature higher than the liquidus line, where the WC–Co based hardmetals are mainly consist of Co-based liquid phase and WC solid grains [3]. The mechanical properties of WC–Co hardmetals strongly depend on the fineness of WC grains, so controlling WC grain growth during liquid phase sintering is one of the major research topics in the field of hardmetals. There are some techniques to control the WC grain growth, for example, adding other carbides such as VC and Cr_2C_3 [4–6], controlling carbon content in the hardmetals [7,8], and controlling the sintering temperature.

Doping other carbides, especially doping VC, is well known as one of the most effective techniques to control a grain growth. Many studies have been devoted to investigate the effect of other carbides doping on WC grain sizes [9,10], grain shapes [11,12] and interface structures [13–15], however, the detail of grain growth inhibition mechanism remains elusive. One reason is the cooling rate effect. The WC grain/Co phase interface structures vary by changing cooling rate after sintering [16]. This was a big problem because the grain growth is thought to be inhibited by the $(W,V)C_x$ phase formed at the WC grain/Co phase interfaces. The interface structures on the sintering state should be observed to understand the authentic grain growth mechanism, but such observation is impossible in slowly cooled specimens. Recently, we found that the cooling rate of oil quenching method is fast enough to freeze up the WC grain/Co phase interface structures on the sintering state [17]. By using this oil quenching technique, we revealed that the $(W,V)C_x$ at the WC (0001)/Co forms nano-dots accompanied by planar $(W,V)C_x$ sheets at the sintering temperature [18]. Such structure is formed by lattice mismatch between $(W,V)C_x$ and WC (0001), so the interface structure can be optimized to improve grain growth inhibition effect by controlling the lattice mismatch.

The lattice mismatch between $(W,V)C_x$ and WC (0001) can be controlled by controlling carbon content in the hardmetals. The lattice constant of $(W,V)C_x$ depends on the composition of itself, and the composition of $(W,V)C_x$ depends on the carbon content in the hardmetals. In this study, we have precisely controlled the carbon content in the VC-doped WC–Co hardmetals and the atomic structure at the WC grain/Co phase interfaces is observed. The VC-doped WC–Co hardmetals with various carbon contents were prepared by oil-quenching subsequently

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http://dx.doi.org/10.1016/j.ijrmhm.2015.07.002
0263-4368/

Table 1
Magnetic saturation and W compositions in Co phase.

	Low carbon	Middle carbon	High carbon
4πσ (kgf)	179.6	201.9	227.7
W in Co (wt.%)	26.33	20.18	12.02

to the liquid phase sintering, and their microstructures were investigated by high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) by using a transmission electron microscope (TEM). From these observations, the proper tactics to improve grain growth inhibition effect will be proposed.

2. Experimental procedure

The VC-doped WC–Co hardmetals were prepared by the ordinal liquid phase sintering method. The base composition of the all hardmetals were WC–12 wt.% Co–0.5 wt.% VC. The carbon content was varied from the lower limit of the three phase region of WC grains, Co based liquid phase and $(W,V)C_x$ to the higher limit in three steps. Each sample is named low carbon (LC), middle carbon (MC) and high carbon (HC). Raw powders of WC (Japan New Metals Co. Ltd., nominal grain size of 0.8 μm), Co (Umicore Co. Ltd., 1.4 μm) and VC (Starck Co. Ltd., 1.6 μm) were weighed to be the target composition, and then they were attritor milled, dried and pressed into $16 \times 16 \times 5$ mm^3 sized green compacts under a pressure of 150 MPa. The carbon content was controlled by adding C powders to the raw powders. The green compacts were divided into four pieces to improve quenching rate. The divided green compacts were liquid phase sintered at 1653 K for 1 h in vacuum better than 1×10^{-2} Pa. After soaking at the sintering temperature, the samples were oil quenched by dropping them into oil. The quenching process was carried out without gas introduction or any other special process and the quenching rate is high enough for freezing up the interface structure at the sintering temperature [17]. The samples were confirmed to be in target composition by saturated magnetization measurements, scanning electron microscopy (SEM, H-S800, Hitachi Co. Ltd., Japan) observations and TEM–EDS analysis. The results are summarized in Table 1. Both saturated magnetizations and W contents in liquid phase correspond to the value in the three phase region of the W–V–C–Co quaternary phase diagram [3,19]. Carbon content is also confirmed to be successfully varied.

The microstructures were investigated by conventional TEM (JEM-2010HC, JEOL Ltd. Japan) and HRTEMs (JEM-4010, JEOL Ltd. Japan, and JEM-2010F, JEOL Ltd., Japan). The composition was analyzed by a twin EDS system (Voyager III, Noran, USA) mounted on an analytical TEM (EM-002BF, Topcon Co., Japan). Thin foils for TEM observations were prepared by mechanical thinning and ion milling with Ar ion beam.

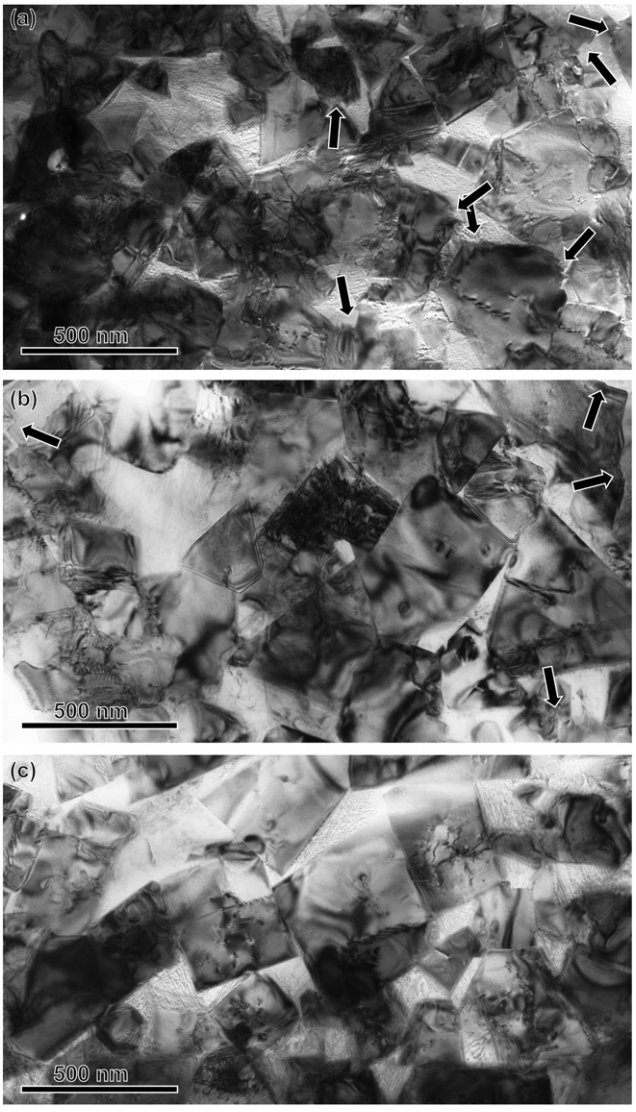

Fig. 2. Typical bright field TEM images of (a) LC, (b) MC and (c) HC. All images are shown in the same scale. The arrows indicate the nano-steps.

3. Results

3.1. Structural and chemical compositional analyses in micro-meter scale

Typical SEM micrographs of LC, MC and HC are compared in Fig. 1. The magnifications of all three images are the same. Gray regions represent WC grains and black regions are Co-based liquid phase. No fourth

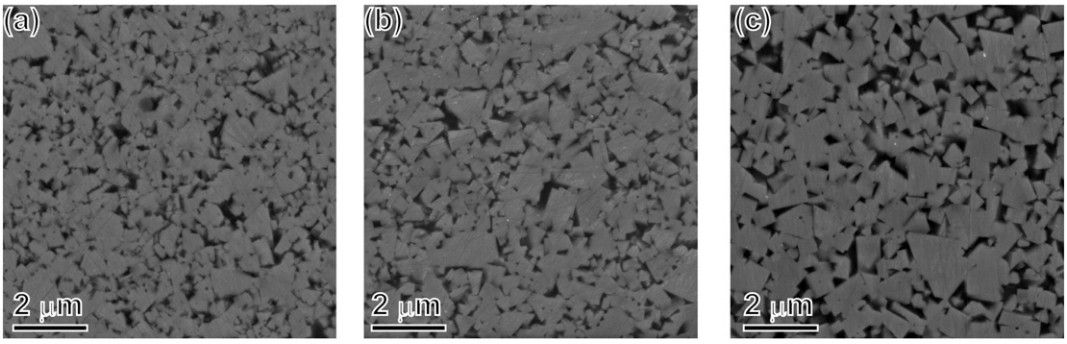

Fig. 1. SEM images of (a) LC, (b) MC and (c) HC. All images are shown in the same scale. Gray regions are WC grains and black regions are Co phases.