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Effect of boron on the microstructure of spark plasma sintered Ultrafine WC

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ABSTRACT

The microstructure of sintered carbide compacts generally contain facetted and abnormally grown grains. In the present work we show that the addition of a small quantity of boron to tungsten carbide powders can induce isotropic coarsening without any abnormal grain growth. The ability of boron to reduce faceting is brought about by the oxidation of boron at low temperatures which leads to isotropic wetting and roughening of particle boundaries during sinter-coarsening at elevated temperatures. Increase in boron content leads to enhanced grain growth and a limiting value to the boron concentration is suggested. Increase in the ambient pressure during sintering increases oxidation of boron and also the sintering temperature leading to a change in both grain shape and size. The isotropic coarsening behavior of WC in the presence of boron conforms to Jackson's theory of crystal growth based on the energetics of a rough liquid–solid interface.

1. Introduction

Sintered compacts of the early transition metal carbides are generally characterized by high hardness and strength and consequently they are often used in the cutting and drilling of rocks and other hard materials. A substantial amount of the carbides used in such mechanically exacting environments belong to the tungsten carbide (WC) family. Cermets based on WC (WC–Co, WC–Ti–Co, WC–TaC–Co, WC–TiC–TaC–Co, WC–Fe, WC–Ni etc.) find use in various industrial products connected with abrasion and wear resistant applications. The microstructures of such sintered compacts of WC are usually fraught with facetted and abnormally grown grains [1–3]. Anisotropic grain morphologies generally result in either an enhancement or degradation of certain desired mechanical properties. For instance, in some cases anisotropic abnormal grain growth (AGG) has been reported to be beneficial in improving the toughness of the hard carbide although generally it is reported to be a disadvantageous attribute when found in nano grained carbides [4,5]. Crystal growth theories predict that faceting is a preliminary step to AGG implying that AGG can be prevented if grain faceting can be avoided during coarsening. However, almost all reports on sintered WC show that they have a strong tendency to form facets due to differences in the surface energies of the prismatic and basal planes and therefore some grains naturally grow abnormally [6,7]. In the present study we show that spark plasma sintered (SPS) compacts of nano tungsten carbide (*n*-WC) can exhibit isotropic grain growth in the presence of boron. While AGG is almost completely suppressed, faceting is also reduced to a great extent. We also study the effect of ambient pressure on the microstructure of the compacts.

2. Experimental details

Commercially purchased *n*-WC powders (~70 nm) were used for sintering. The WC powder was mixed with 1, 2 or 4 wt.% B in a planetary ball milling unit for 30 min. Approximately 2.5–3 g of these powders was filled into a 10 mm diametric graphite die for spark plasma sintering (SPS). Carbon spacers were used to separate the powder sample from the punch and die. After initial temperature stabilization at 873 K for 3 min, sintering was carried out in vacuum (<4 Pa) at a constant heating rate of 150 K/min and a compressive stress of 40 MPa. The first set of samples (sample set I) was prepared with the 1 wt.% B powder by interrupting the sintering process at various temperatures to study the sintering and microstructure evolution. The second set of samples (set II) was prepared uninterrupted until completion of sintering with the same 1 wt% B powder and under the same heating conditions except that atmospheric air was leaked into the chamber during sintering in a controlled manner such that the guage pressure was 6 Pa, 10 Pa and 25 Pa in three experiments. Similarly a third set (set

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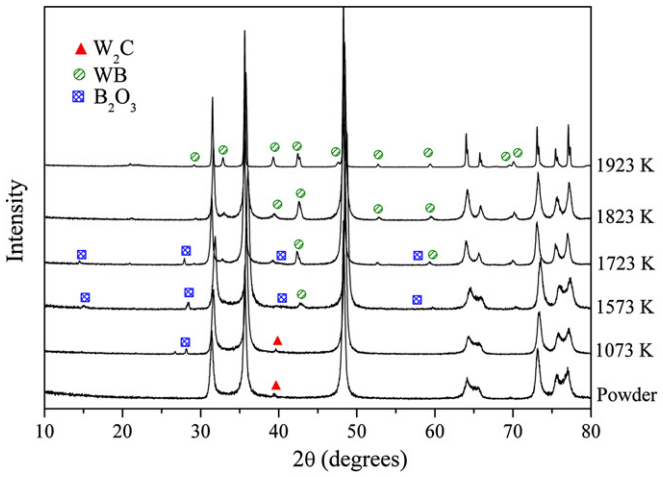

Fig. 1. XRD of WC-1% B samples interrupted at various temperatures.

III) was prepared with the 2 and 4 wt% B samples but with ambient pressures of 4 and 25 Pa and with the same heating rate. Grain sizes were measured by fracturing the specimens and delineating the grain boundaries using an image analysis software (Image Pro). Approximately 50–100 grains from three different regions of the compacts were considered for evaluation and the average values are reported. Samples for TEM were prepared by the usual routine of mechanical polishing, dimpling and Precision Ion Polishing (PIP) with Ar ions.

3. Results and discussion

Interrupted sintering experiments (sample set I) showed that the WC-1% B samples underwent oxidation of boron into B_2O_3 even at very low temperatures (1073 K) and persists until 1723 K as shown in Fig. 1. Around 1573 K the WB phase nucleated and was found to persist until the end of sintering. Above 1723 K, the volatile B_2O_3 phase completely evaporated leaving a microstructure comprised of only WC and WB. Observation of the microstructure revealed that the transformation into well formed grains occurs at a temperature of 1673–1723 K. Between 1823 and 1973 K, rapid grain growth was observed. The grains were found to be almost isotropic without any AGG in the microstructure. The pores, on the other hand, were isolated and circular, lying at the grain boundaries or at the triple grain junctions. However, the cross-sectioned surface at 1073 K clearly revealed a large volume fraction of a thin glassy liquid layer over the WC particles. Subsequent EPMA analyses of these samples confirmed that they were boron oxide layers (Fig. 2). It is suspected that during the process of ball milling, the edges of the large B particles were broken into smaller pieces that intially oxidized. Subsequently they evaporated owing to the high vapor pressure of B_2O_3. Faceting of grains was indeed observed in the TEM specimens. But they were mostly confined to those grain junctions that were unwetted by the B_2O_3 phase. In particular, the Σ2 grain boundaries (grain intersections with a 90° rotation about the [10$\bar{1}$0]) axis were relatively intact with sharp facets confirming the low energy nature of these types of grain boundaries [8] (Fig. 3).

The second set of samples (set II) prepared at various levels of ambient pressure showed an increase in sintering temperature with the pressure. A corresponding increase in grain size was also observed (Fig. 4). Increase in ambient pressure results in a higher fraction of B_2O_3 in the microstructure. A corresponding increase in grain size indicates the influence of both the liquid oxide phase and sintering temperature on the dissolution – reprecipitation process of grain coarsening. Finally, increase in boron content (set III) resulted in a proportional increase in the grain size of the sintered compacts (Fig. 5). At higher ambient pressures, the grain sizes also increased, but to a lesser extent. The grain shapes were more 'rounded' and the fraction of the WB phase also increased proportional to the B content.

The influence of boron on both grain size and the grain shape points to a strong influence not only on the dissolution – reprecipitation process but also on the interface energy of the liquid–solid interface. The melting point of pure B is 2365 K which is slightly higher than the present experimental temperatures reached (2073 K). However, in SPS the measured temperatures are usually lower by a factor of 100–200 K as compared to the local temperature inside the specimen owing to intense over-heating at the particle boundaries and also due to the temperature gradient across

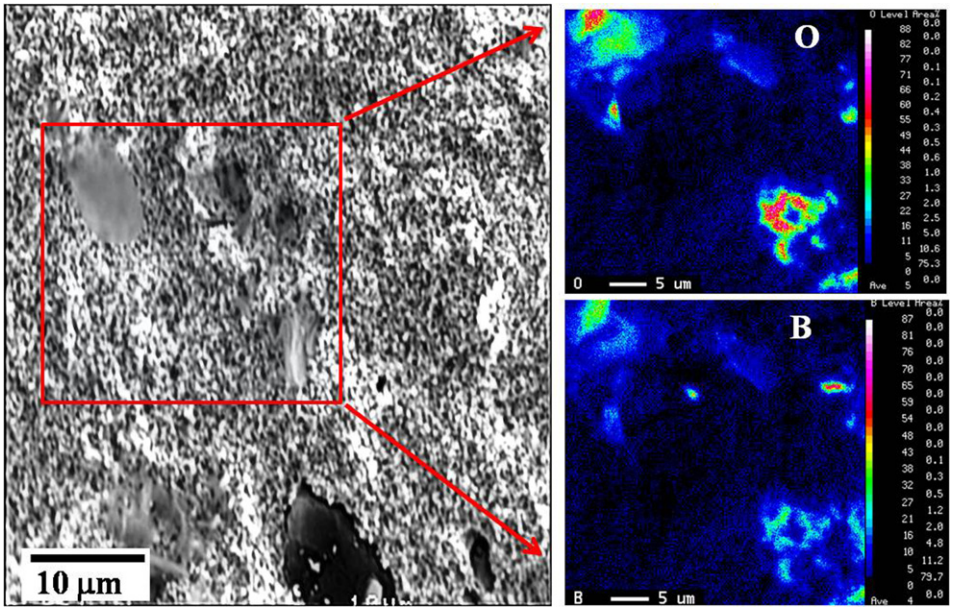

Fig. 2. EPMA composition map of a sample sintered at 1073 K showing the distribution of B and O.