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Effect of boron addition on sintering of tungsten based alloys

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Tungsten based heavy alloys typically consist of W as a major phase and a combination of two or more relatively low melting point transition metal additives such as Ni, Fe, Cu and Co. These alloys are consolidated by liquid phase sintering. Alloy design in tungsten based alloys is done to improve strength, ductility, toughness, or to produce tailored composite properties. Tungsten based alloys benefit from their composite nature since they have high strength and hardness from the *bcc* tungsten and ductility from the *fcc* matrix phase. Extensive work has been carried out in the past on liquid phase sintering of tungsten heavy alloys [1–3]. Typical tensile strengths range from 700 to 1800 MPa for liquid phase sintered alloys containing 90 to 98 wt% W and up to 30% ductility can be achieved in these alloys depending on W content, matrix composition and processing schedule. The most popular tungsten based alloys consist of mixed elemental powders of W, Ni and Fe, where the W content typically varies from 88 to 98 wt%, the balance being the matrix phase. The selection of Ni and Fe in the ratio 7:3 effectively prevents the formation of brittle intermetallic phases. Several researchers have examined the effect of modified binder additives on the sintering behavior and mechanical properties of tungsten alloys [4, 5].

The present work focuses on the processing of novel tungsten based alloys with NiB and/or FeB additions and their microstructural characterization as well as hardness measurements. It is envisaged that B addition will result in a lowering of the solidus temperature; thereby enhancing the melt effectiveness for densification during sintering. Addition of boron in either elemental form or as a compound (for example, Fe_2B, BN, NiB, and CrB) has been proved to be beneficial as a sintering aid for ferrous alloys [6–8]. Elemental B is susceptible to oxidation [9]. Hence, in this study, B was added as NiB and FeB.

The tungsten powder in as-reduced form (Grade: M55) was supplied by Osram Sylvania (Towanda, PA, USA). The powder had an average size of 5.5 μm and irregular morphology. Compositions of tungsten based alloys containing NiB and/or FeB were prepared by mixing in a turbula mixer for 30 min. In all, seven compositions were investigated in the present study. The base composition selected for this study was 90W-7Ni-3Fe (wt%). Cylindrical green compacts of 12.7 mm diameter and about 5 mm height were prepared using a uniaxial hydraulic press (Apex Construction Ltd., UK) at a compaction pressure of 200 MPa. The sintering of green compacts was carried out at 1500 °C in a super-Kanthal heated tubular furnace (OKAY 70T-4, Bysakh & Co., India) in hydrogen (dew point: −35 °C) with a flow rate of 1 l/min. The compacts were heated at 5 °C/min and the samples were held at the sintering temperatures for 60 min. Subsequently, the samples were furnace cooled. The compact sintered density was determined using both the dimensional measurement as well as water displacement method. The sintered density for each composition was normalized with respect to its theoretical density which was calculated using the inverse rule of mixture.

The microstructures of as-polished samples were examined using a Leica optical microscope with digital image acquisition capability. The quantitative analysis of W content in the matrix for all samples was carried out using an electron probe microanalyser (EPMA) (Jeol, JXA-8600SX Superprobe, Japan) equipped with wave dispersive X-ray spectroscopy WDS. The operating conditions such as magnification (1000×), spot size (2 μm), probe current (5×10^{-8} A), working distance, tilt angle and take-off angle of the two microscopes were all kept constant for all measurements.

Bulk hardness measurements were performed on polished surfaces at 2 kg load using a Vickers hardness tester (Leco, V-100-C1). The observed hardness values are mean values of five readings taken at random locations throughout the sample. A micro-hardness tester (Leitz 8299, Germany) was used to evaluate the tungsten grains and matrix phase. The micro-hardness measurements on the matrix and the tungsten grains were conducted at 5 and 50 g load, respectively.

Table I summarizes the variation in sintered density with respect to the composition of the matrix. It is evident that near theoretical density is achieved in the W-7Ni-3FeB alloy. Note that for the W powder size (5.5 μm), which is relatively coarse, the base composition (90W-7Ni-3Fe alloy) achieved only 97% of its theoretical density during liquid phase sintering. Of the tailored compositions, the W-7NiB-3FeB alloy attained the lowest sintered density (90% of theoretical density). The other composition of interest is W-7NiB-3Fe, because it achieved 96% of its theoretical density. Typically, at about 90% or more sintered density the porosity is expected to be predominantly closed type. Such closed residual pores can be removed through post-sintering operations, such as HIPing. The melting point of NiB is 1018 °C, whereas that of FeB is 1650 °C. Though the melting point of FeB is high, it is lowered

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TABLE I Summary of alloy compositions (in wt%), sintered density, solubility of W in the matrix, and hardness

Alloy composition (wt%)	Sintered density (% theoretical)	W content in the matrix (wt%)	Bulk hardness, HV_2	Micro hardness	
				W ($HV_{0.05}$)	Matrix ($HV_{0.005}$)
W-7Ni-3Fe	97	24 ± 0.4	354 ± 13.5	457 ± 12	137 ± 14
W-7NiB-3Fe	96	21 ± 02	412 ± 48	448 ± 5	130 ± 9
W-7Ni-3FeB	99	24 ± 1.4	340 ± 14	477 ± 13	142 ± 15
W-7NiB-3FeB	90	20 ± 0.8	458 ± 64	457 ± 9	164 ± 15
W-7[Ni-NiB(50:50)]-3Fe	94	23 ± 1.1	329 ± 12	487 ± 7	104 ± 4
W-7Ni-3[Fe-FeB(50:50)]	91	23 ± 1.2	353 ± 14	473 ± 15	122 ± 6
W-7[Ni-NiB(50:50)]-3[Fe-FeB(50:50)]	94	22 ± 1.7	357 ± 30	447 ± 8	127 ± 12

by the addition of Fe. Likewise, it is expected that Ni additions will have a similar effect in depressing the melting point of FeB. In contrast, addition of Ni leads to an increase in the melting point of NiB. However, the liquidus temperature remains well below the melting point of Ni. For the composition W-7NiB-3FeB, the absence of any Ni or Fe implies that FeB would have remained in the solid-state and that the densification contribution during liquid phase sintering is due to the melting of the NiB phase alone. Other compositions show higher sintered densities as they contain Ni and/or Fe.

The optical micrographs of typical microstructures of the samples are shown in Fig. 1. All alloys except W-7NiB-3FeB show a typical liquid phase sintered microstructure which is associated with rounded W grain morphology and homogenous distribution of binder phase. In contrast, the W-7NiB-3FeB shows relatively smaller and irregular W grain. In addition, the W grains in W-7NiB-3FeB exhibit significant coalescence, which is indicative of the non-uniform distribution of the liquid phase during sintering. The EPMA analyses on the W-Ni-Fe and B-modified tungsten heavy alloy composition shows 20–25 wt% tungsten solubility in the matrix (Table I). As expected, of all the alloys, W-7NiB-3FeB alloy has the least W solubility (20 wt%) in the matrix. This implies less solution reprecipitation during sintering and results in smaller and more irregular W grain morphology. The bulk hardness for the tungsten alloys are presented in Table I. It is observed that the alloy W-7NiB-3FeB has the highest hardness, followed by W-7NiB-3Fe. Despite having the least sintered density, the high hardness in W-7NiB-3FeB alloy can be attributed to the lower W grain size. Furthermore, note the high standard deviation in the measured hardness of W-7NiB-3FeB, which implies an inhomogeneous microstructure. Table I also presents the micro-hardness of the matrix phase and the tungsten grains. The W-7NiB-3FeB alloy matrix exhibits maximum micro-hardness which would also contribute to enhancing the overall bulk hardness of the alloys.

In summary, this study demonstrates the role of boron addition in the form of NiB or FeB on the consolidation of tungsten-based alloys (containing 90 wt% W) through liquid phase sintering for various tailored compositions. Of all the compositions, the W-7Ni-3FeB alloy achieves highest density during sintering and consequently results in appreciable hardness. About 20 to

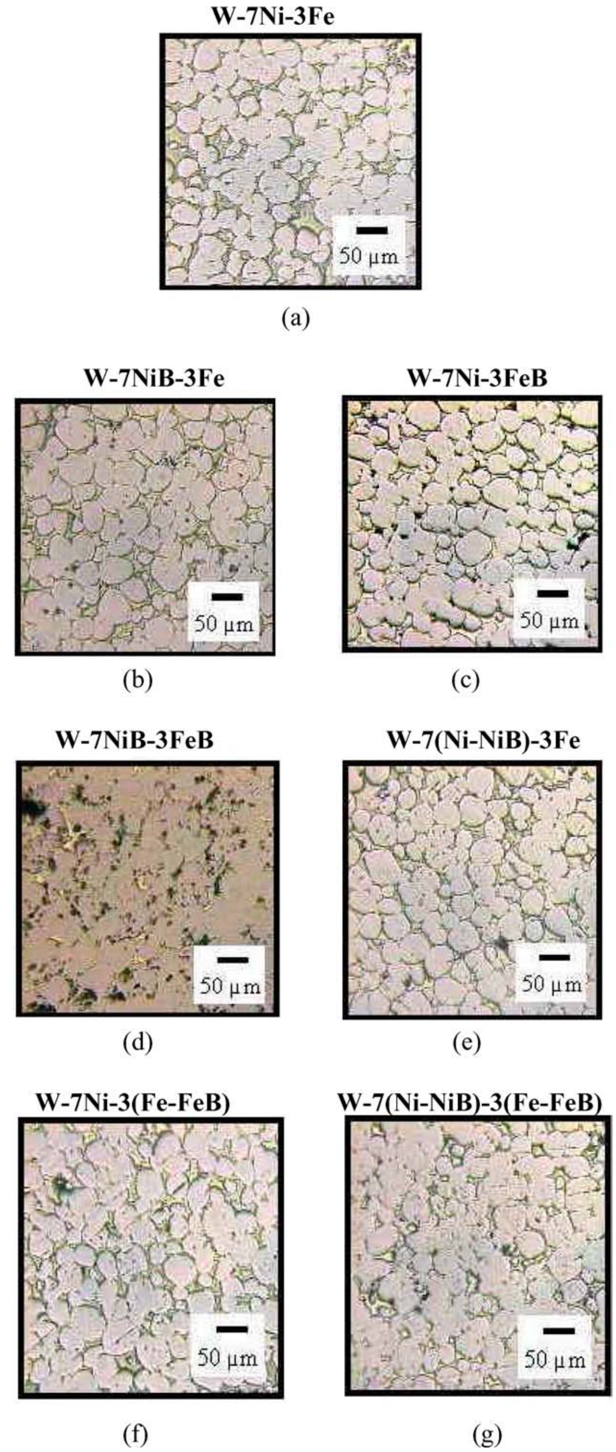

Figure 1 Optical microstructures of tungsten based alloys liquid phase sintered at 1500 °C.

25 wt% tungsten solubility in the B-modified matrix is observed for the investigated alloys which is comparable that in the W-Ni-Fe alloys. Both, the B-modified W alloys as well as W-Ni-Fe alloys have similar microstructure which is indicative of similar sintering phenomenology in both. The hardness of B-added compositions is similar and in some cases even higher as compared to the 90W-7Ni-3Fe alloy.

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