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Pseudopartial wetting of W/W grain boundaries by the nickel-rich layers

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ABSTRACT

The excellent properties of heavy tungsten-based alloys are based on the combination of hardness of W grains, as well on the toughness and ductility of the binder with low melting temperature (usually containing nickel, iron, or copper). The topology (and resulting properties) of binder network are controlled by the complete and incomplete wetting of W/W grain boundaries (GBs) and GB triple junctions (TJ). We observed for the first time that pseudoincomplete (or pseudopartial, or frustrated complete) GB wetting by Ni layers is also present in W–Ni alloys. Namely, the channel of a Ni-rich solid solution in GB TJ forms the non-zero dihedral contact angle not only with "dry" W/W GBs (incomplete GB wetting), but also with W/W GBs containing the uniformly thin (3 nm) Ni-rich layer (pseudoincomplete GB wetting).

1. Introduction

Pure tungsten is expensive and difficult to machine and manufacture. Therefore, the heavy tungsten-based alloys were developed which maintain some of the useful characteristics of tungsten, such as density and X-ray shielding capabilities, but which would be easier to machine and less expensive. Such heavy tungsten alloys are used as weights, for ballast for vibration and kickback reduction, as X-ray shields and ion beam apertures as well as aircraft bucking bars. They contain about 90% or more tungsten with nickel, iron, or copper added [1]. Exactly these additions ensure the high workability of W-based alloys. It is because the ductile low-melting binder is distributed between the hard W grains.

The distribution of Ni, Fe or Cu-rich binder in the W/W grain boundaries (GBs) is formed during the liquid-phase or activated sintering as well as post-sintering processing and is governed by the GB wetting phenomena. Reviews of GB wetting phenomena can be found in [2–6]. It is important to underline here that GB wetting phase can be not only liquid but also solid [7,8]. In case of W-based alloys the GB wetting by a melt controls the liquid-phase sintering and GB wetting by a second solid phase controls the activated sintering. It is because the activated sintering of tungsten-based alloys takes place at the temperatures where only solid phases exist [9–13].

One distinguishes the GB complete (CW) and partial (PW) or incomplete wetting [14,15]. However, in certain conditions the so-called pseudopartial (PPW) or pseudoincomplete, or frustrated complete GB wetting appears in a phase diagram between complete and partial wetting [16]. In case of pseudopartial GB wetting, the thin GB layer can coexist with large droplets (or particles) of the wetting phase with a non-zero dihedral (contact) angle $\theta > 0$. Thus, such intergranular films (IGFs) can be observed in the two-phase (or multiphase) fields of bulk phase diagrams, in the broad intervals of concentration, temperature and/or pressure. The IGFs driven by the pseudopartial GB wetting can drastically modify the properties of polycrystals, in particular those of technologically important Fe–Nd–B-based hard magnetic alloys [17], WC–Co cemented carbides [18] and Al-based light alloys [19,20]. The W–Ni alloys also can contain the few nm thin Ni-rich IGFs [21]. The goal if this work is to clarify, whether such IGFs can appear in the W–Ni alloys due to the pseudoincomplete GB wetting.

2. Experimental

The experiments were performed on sintered tungsten-nickel material supplied by Metallwerke Plansee. The nominal purity of W was 99.98 wt%, C(15), Fe(20), Mo(40), and P(20) being the major impurities (in wt. ppm). The purity of nickel was 99.99 wt%. After

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sintering the samples have a cylindrical shape with diameter of 10 mm and height of 8 mm. The Ni content in the specimens was measured by atom absorption spectroscopy in a Perkin-Elmer spectrometer (model 5000). The composition of alloy was W – 0.3 wt% Ni. The sintered cylinders were cut with spark erosion into elongated samples with 2 × 2 mm section, which were chemically polished and were then sealed into evacuated (a residual pressure of 4×10^{-4} Pa) quartz ampoules. After that, the ampoules were annealed in a muffle furnace at temperatures of 1050 °C for 190 h. This annealing time is at least 10 times longer than typical duration of activated sintering of W-based alloys [9,11–13]. After annealing, the samples were quenched in water. The samples preparation for transition electron microscopy (TEM) studies was carried out on the FEI Strata 400S dual beam facility. The microstructure of the samples was characterized using an aberration corrected TITAN 80–300 transmission electron microscope.

3. Results and discussion

Fig. 1a shows the microstructure of W–Ni alloy annealed at 1050 °C. Two GB triple junctions and five GBs are visible. In TJ2 (left-hand side) all three GBs form the non-zero dihedral (contact) angles with the channel of Ni-rich phase in TJ (namely, θ = 81°, 57° and 34°). In TJ1 (right-hand side) the GB1 forms the non-zero contact angle θ = 39° and other two GBs form zero contact angle with the channel of Ni-rich phase in TJ1. Arrows in Fig. 1a indicate direction across the grain boundaries for which the elemental profiles have been obtained. Result of the EDS elemental profiling is shown in Fig 1b (GB1) and Fig. 1c (GB2). According to these plots, grain boundary layer of (Ni) phase is observed. The thickness of this layer is ~12 nm for GB1 (θ = 0° in TJ1) and ~3 nm for GB2 (θ = 39° in TJ1 and θ = 57° in TJ2). HRTEM image of GB2 also reveals the presence of thin (Ni) phase layer along GB2 (Fig. 2). It has a uniform thickness of ~3 nm along all the length of GB2. Thus, indeed, the GB thin films of Ni-rich films can coexist with non-zero GB contact angle with a second phase.

In the majority of cases the direct transition occurs from partial (θ > 0) into complete (θ = 0) wetting, for example by increasing temperature [14,15] or decreasing pressure [22]. However, in some cases the state of pseudopartial wetting occurs between partial and complete wetting. In this case the contact (dihedral) angle θ > 0, the liquid droplet does not spread between the grains, but a thin (few nm) precursor film forms around the droplet and separates both abutting grains. Such a precursor film is very similar for the liquid "pancake" in case of complete wetting and deficit of the liquid phase [4,23]. The sequence of discontinuous PW ↔ PPW and continuous PPW ↔ CW transitions was observed for the first time in the alcanes/water mixture [24]. The first direct measurement of the contact angle in the intermediate wetting state (PPW) was performed in the sequential-wetting scenario of hexane on salt brine [25]. Later on the formation of Pb, Bi and binary Pb–Bi precursors surrounding liquid or solidified droplets was observed on the surface of solid copper [26].

In a classic case, wetting or prewetting IGFs only exist close to the solidus line of a bulk phase diagram. On the contrary, the IGFs connected with pseudopartial GB wetting can be observed in a broader range of phase fields in binary and muticomponent phase diagrams, including two- and multiphase regions, coexisting with

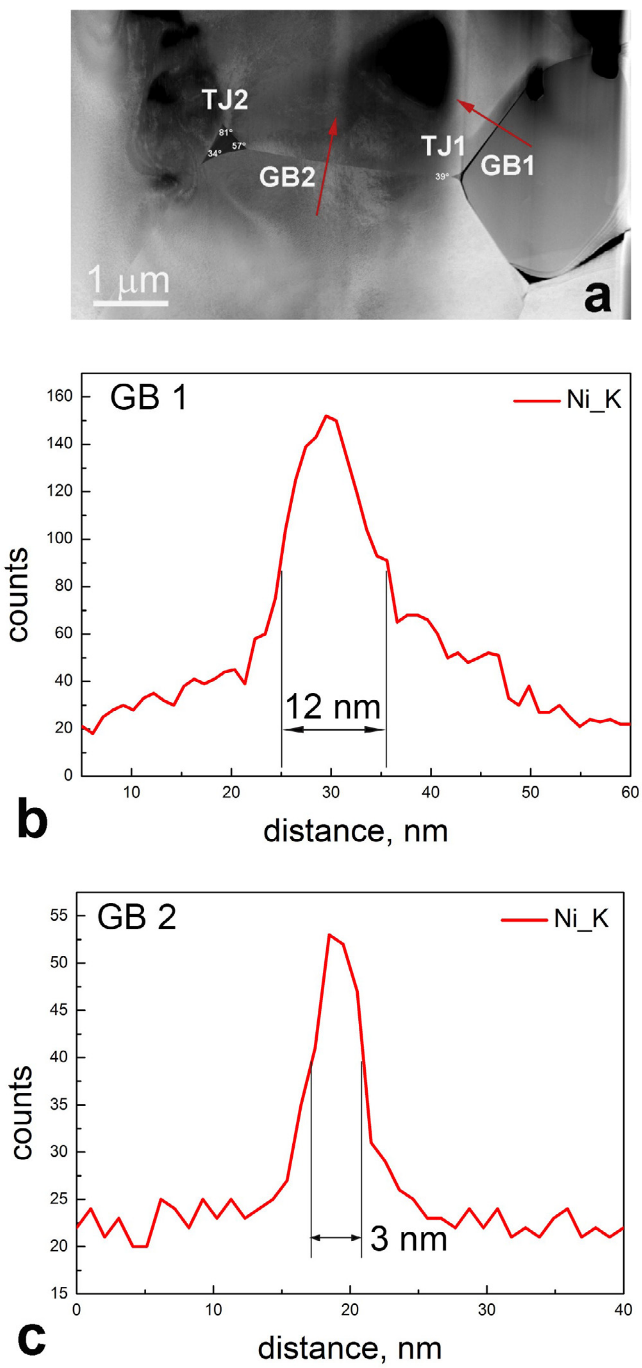

Fig. 1. STEM HAADF image of the W–Ni alloy annealed at 1050 °C. Arrows denote the directions of the elemental profiles (b and c) across the grain boundaries.

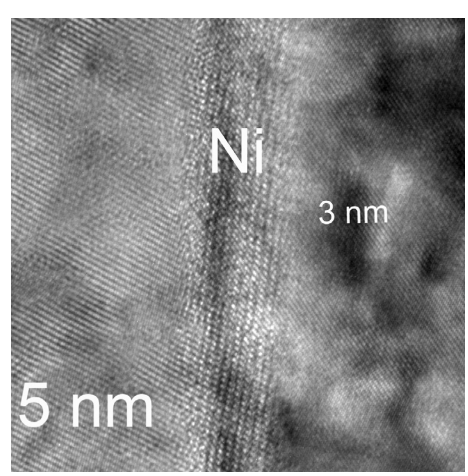

Fig. 2. HRTEM image of the GB2 (see Fig. 1a); 3 nm thick Ni layer is visible between two tungsten grains.

the pseudopartial-wetting phases that form non-zero contact (dihedral) contacts where they meet the pseudopartial-wetting complexions. Therefore, such IGFs can be used as a fine instrument for the so-called grain boundary engineering (term first introduced by Tadao Watanabe [27]). As we saw, the thin IGFs can improve the magnetic properties (Fe–Nd–B-based hard magnetic alloys) [17], fracture toughness and strength (WC–Co cemented carbides) [18] or formability (Al-based light alloys) [19,20]. We observed in this work that such IGFs, driven by the pseudoincomplete GB wetting, exist also in the W–Ni alloys. They can explain, for example, the peculiarities of GB diffusion in W-based alloys [9,10] and quick activated sintering of W–Ni alloys [11–13].

4. Conclusions

The key to the exceptional properties of heavy tungsten-based alloys is the optimal combination of hardness of W grains, as well the toughness and ductility of the binder with low melting temperature. We observed that the topology (and resulting properties) of binder network are controlled by the complete and incomplete wetting of W/W grain boundaries (GBs) and GB triple junctions. We also observed for the first time that pseudoincomplete wetting of W/W GBs by Ni layers is also present. Namely, the channel of Ni-rich binder in GB TJ forms the non-zero dihedral contact angle not only with “dry” W/W GBs (incomplete GB wetting), but also with W/W GBs containing the uniformly thin (3 nm) Ni-rich layer (pseudoincomplete GB wetting).

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