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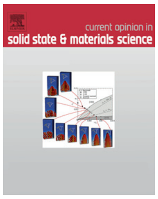

Grain boundary complexions and pseudopartial wetting

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ABSTRACT

The important class of grain boundary (GB) complexions includes the few nanometer thick layers having composition which strongly differs from that of the abutting grains. Such GB complexions are frequently called intergranular films (IGFs) and can be observed close to the lines of wetting, prewetting and premelting complexion transitions in the bulk phase diagrams. In the majority of systems, the direct transition between complete and partial GB wetting takes place (by changing temperature, pressure, etc.). However, in certain conditions the so-called pseudopartial (or pseudoincomplete, or frustrated complete) GB wetting appears in a phase diagram between complete and partial wetting. In case of pseudopartial GB wetting, the thin GB layer of a complexion (IGF or 2-D interfacial phase) can coexist with large droplets (or particles) of the wetting phase with a non-zero dihedral (contact) angle. Thus, such IGFs can be observed in the two-phase (or multiphase) fields of bulk phase diagrams, in the broad intervals of concentrations, temperature and/or pressure. The IGFs driven by the pseudopartial GB wetting can drastically modify the properties of polycrystals. In this review, we discuss this phenomenon for the technologically important Fe–Nd–B-based hard magnetic alloys, WC–Co cemented carbides and Al-based light alloys.

1. Introduction

The developments of last decade show that properties of fine-grained and nanograined materials are critically controlled by the behaviour of grain boundaries (GBs) and triple junctions (TJs) [1–4]. Moreover, the most advanced experimental methods like high-resolution electron microscopy (HREM) and atom probe microscopy allowed observing that GBs and TJs are frequently not atomically thin and smooth but contain the few nm thick layers or so-called intergranular films (IGFs) [3–21]. Such IGFs form the important class of grain boundary complexions [5,6,21] having composition which strongly differs from that of the abutting grains. These layers can appear in equilibrium, non-equilibrium (transient) or steady-state structures [4–20,22–31]. In the majority of cases such surface and GB complexions are intimately connected with GB wetting, prewetting and premelting equilibrium complexion transformations (for review see [5,6] and references therein). Such GB transformations were first predicted in seminal works of Cahn [32] and Ebner and Saam [33]. They analysed the transition between complete (CW, Fig. 1c, d, and g) and partial (PW, Fig. 1a, b, and g) wetting close to the critical point in a two-component phase diagram. However, most interestingly, from our point of view, is the phenomenon of the so-called pseudopartial (or pseudoincomplete, or frustrated complete [34]) GB wetting (Fig. 1e and f) marked as PPW in the generic phase diagram (Fig. 1g proposed in Ref. [35]) [36–39]. The pseudopartial GB wetting is intermediate between complete (Fig. 1d) and partial (Fig. 1b) GB wetting. PPW was first predicted by de Gennes [40]. De Gennes analysed the influence of the so-called Hamaker constant on wetting phenomena [40]. In case of pseudopartial GB wetting, thin GB layer of a second phase (i.e. IGF or complexion) can coexist with droplets (or particles) of a second phase with large non-zero contact (dihedral) angle (Fig. 1f). It means that such IGFs or GB complexions of high adsorption levels can be observed in the two-phase (or multiphase) fields of bulk phase diagrams (in addition to the single phase regions), i.e. in the broad ranges of concentrations, temperature and/or pressure. The IGFs can drastically modify the properties of polycrystals.

In this review we will demonstrate the presence of pseudopartial GB wetting for technologically important Fe–Nd–B-based hard magnetic alloys [41,42], WC–Co cemented carbides [39] and Al–Zn light alloys [37,38]. The IGFs of Nd-rich phase magnetically isolate the $Nd_2Fe_{14}B$ grains from each other and make Fe–Nd–B-based alloys the best known hard magnetic alloys with highest magnetic energy product HB (B being the flux density and H being the field

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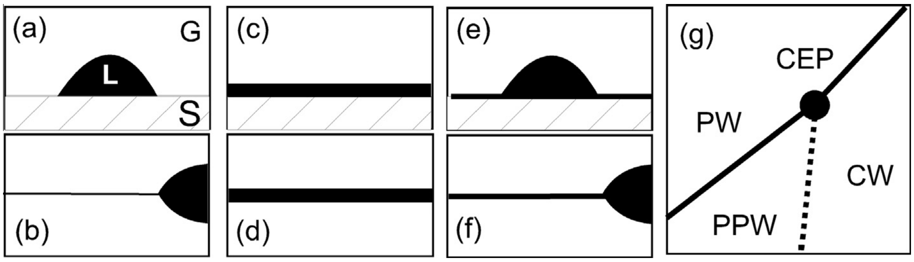

Fig. 1. The schemes for the wetting of free surfaces and GBs. (a) partial surface wetting, L – liquid phase, S – solid phase, G – gas phase; (b) partial GB wetting; (c) complete surface wetting; (d) complete GB wetting; (e) pseudopartial surface wetting; (f) pseudopartial GB wetting; (g) generic wetting phase diagram [33], PW – partial wetting, CW – complete wetting, PPW – pseudopartial wetting, CEP – critical end point, thick lines mark the discontinuous (first order) wetting transition, thin dotted line mark the continuous (second order) wetting transition.

strength) [43,44]. Thin IGFs of Co binder form the ductile skeleton between grains of hard tungsten carbide and ensure their unique combination of high hardness, wear-resistance, toughness and strength [39,45–47]. The 2–4 nm thin Zn-rich layers (complexions) between Al grains cause superductility of the ultrafine-grained Al–Zn alloys obtained by the high pressure torsion [26–28,48,49].

2. Definition of pseudopartial wetting

The pseudopartial (or pseudoincomplete, or frustrated complete) wetting, where the bulk phase of a fluid has a nonzero contact angle on top of a film of the same fluid, has been of interest in the scientific literature since the end of 1980s [34–40,50–53]. Let us consider a partially melted two- or multicomponent polycrystal between solidus temperature T_S and liquidus temperature T_L. Consider the droplet of a liquid phase on the surface of a solid phase or between two solid grains. Usually one distinguishes partial (incomplete) and complete wetting of surfaces or interfaces. In case of complete wetting the contact angle θ is zero. If the contact angle θ is between zero and 180° one speaks about partial or incomplete wetting [6]. We will use further this terminology though in some literature sources one speaks about partial wetting when the contact angle is between 90° and 180°. In these sources one uses “wetting” (meaning complete or perfect wetting) vs. “non-wetting” (including partial wetting, which is “non-wetting” thermodynamically) [6].

If a liquid droplet partially wets a solid surface (Fig. 1a) then $\sigma_{sg} - \sigma_{sl} = \sigma_{lg} \cos\theta$, where σ_{sg} is the free energy of solid/gas interface, σ_{sl} is the free energy of solid/liquid interface, σ_{lg} is that of liquid/gas interface. If a liquid droplet partially wets the boundary between two solid grains (Fig. 1b), then $\sigma_{gb} = 2\,\sigma_{sl} \cos\theta$, where σ_{gb} is the free energy of a grain boundary. The free surface or GB which is not covered by the liquid droplets remains dry and contains only adsorbed atoms of a second component with coverage below one monolayer. In this case the GB can exist in the equilibrium contact with the liquid phase. If $\sigma_{sg} = \sigma_{lg} + \sigma_{sl}$ or $\sigma_{gb} = 2\,\sigma_{sl}$ complete wetting of free surface or grain boundary takes place and θ reaches zero (Fig. 1c and d) [54]. We have to underline here the subtle but important difference between “dry” interfaces and equilibrium interfaces [19,54,55]. In the criteria used above, the terms σ_{sg} and σ_{gb} actually refer to the so-called “dry” or “clean” surface or GB before wetting (without adsorption of the wetting phase) [19,54,55]. However, the wetted surface or GB is the new interface thermodynamically [54]. In the literature, there are two ways to differentiate this subtle, but important, difference. In the surface wetting community, one frequently use σ_{sv} (meaning the solid/vacuum interface) to denote that it is different from the equilibrium σ_{sg} (meaning the equilibrium solid/gas interface, which, at equilibrium, will be wetted so that $\sigma_{sg} = \sigma_{lg} + \sigma_{sl}$ [54]). This notation is difficult to be used for denoting “dry” or “clean” GBs, so other authors use symbols like σ^0_{gb} [19,55] to differentiate “dry” or “clean” GBs from the equilibrium GBs with equilibrium adsorption, disordering or wetting (here wetting means adsorption with infinite GB excess). Thus, in the case $\sigma_{sg} > \sigma_{lg} + \sigma_{sl}$ or $\sigma_{gb} > 2\,\sigma_{sl}$, the contact angle θ also remains zero, and liquid spreads over the free surface or between grains. In this case, a GB separating abutting grains is completely substituted by the liquid phase.

The transition from incomplete to complete (partial) GB wetting proceeds at a certain T_w if the energy of two solid-liquid interfaces $2\,\sigma_{SL}$ becomes lower than the GB energy $\sigma_{GB} > 2\,\sigma_{SL}$. Cahn [32] and Ebner and Saam [33] first showed that the (reversible) transition from incomplete to complete wetting can proceed with increasing temperature, and that it is a true surface phase (complexion) transformation. The GB wetting temperatures T_w, depend both on GB energy and solid-liquid interfacial energy which, in turn, depend on the crystallography of these interfaces [56–59]. The transition from incomplete to complete GB wetting starts at a certain minimum temperature T_{wmin}. T_{wmin} is determined by combination of maximum σ_{GB} and minimum σ_{SL}. The transition from incomplete to complete GB wetting finishes at a maximum temperature T_{wmax}. T_{wmax}, in turn, is determined by combination of minimum σ_{GB} and maximum σ_{SL}. The fraction of completely wetted GBs increases from 0 to 100% as the temperature increases from T_{wmin} to T_{wmax} [60–65]. As a result, the new tie-lines appear in the S + L area of a phase diagram at T_{wmin} and T_{wmax} [60–65].

In case of complete wetting (Fig. 1c and d), $\sigma_{sg} > \sigma_{lg} + \sigma_{sl}$ or $\sigma_{gb} > 2\,\sigma_{sl}$, contact angle θ is zero, and liquid spreads over the free surface or between grains. What happens, if the amount of liquid is small and surface (or GB) area is large? In this case the liquid spreads until the abutting solid grains or solid and gas begin to interact with each other through the liquid layer. The liquid forms a “pancake” with thickness e_s about 2–5 nm [11,66]:

$$e_s = (A/4\pi S)^{1/2}, \tag{1}$$

where $S = \sigma_{sg} - \sigma_{sl} - \sigma_{lg}$ is the spreading coefficient on a strictly “dry” solid and A is the Hamaker constant [40,66]. In case of complete wetting, $A > 0$ and $S > 0$ [40,66]. Such “pancake” (complexion) on the free surface or between two grains is formed by the deficit of a wetting phase. Such conditions can be found in the α + L two-phase area of a phase diagram, but in the narrow “temperature (pressure) - concentration” band very close to the solidus line.

In the majority of cases, the direct transition occurs from partial wetting into complete wetting, for example by increasing temperature [59,67,68] or decreasing pressure [69]. However, in some cases, the pseudopartial wetting (PPW in Fig. 1g) appears between partial and complete wetting. In this case the contact angle θ > 0, the liquid droplet does not spread over the substrate, but the thin (few nm) precursor film exists around the droplet and separates substrate and gas (Fig. 1e). Such thin precursor film (complexion) is very similar to the liquid “pancake” which forms in case of