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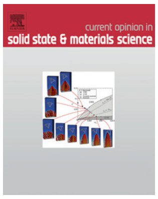

The role of grain boundary energy in grain boundary complexion transitions

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ABSTRACT

Recent findings about the role of the grain boundary energy in complexion transitions are reviewed. Grain boundary energy distributions are most commonly evaluated using measurements of grain boundary thermal grooves. The measurements demonstrate that when a stable high temperature complexion co-exists with a metastable low temperature complexion, the stable complexion has a lower energy. It has also been found that the changes in the grain boundary energy lead to changes in the grain boundary character distribution. Finally, recent experimental observations are consistent with the theoretical prediction that higher energy grain boundaries transform at lower temperatures than relatively lower energy grain boundaries. To better control microstructures developed through grain growth, it is necessary to learn more about the mechanism and kinetics of complexion transitions.

1. Introduction

The characteristic structure and chemical composition of a grain boundary [1], free surface [2], phase boundary [3], or dislocation [4] are referred to as its complexion. Extensive research has shown that grain boundary complexions can abruptly transition from one state to another in response to a change in composition or temperature [5,6]. These transitions are thought to occur because they reduce the grain boundary excess free energy [7]. The purpose of this paper is to review recent findings on the role of the grain boundary energy in complexion transitions. Efforts to measure the change in grain boundary energy associated with a complexion transition will be reviewed and the role of the anisotropy of the grain boundary energy will be discussed. Because the experiments have mostly explored the changes in complexion that occur as a function of temperature, we will begin by reviewing what is known about the effect of temperature on the grain boundary energy. Next, experimental methods to measure the change in energy will be described and the results of those measurements will be reviewed. Experiments probing the influence of grain boundary energy anisotropy will then be discussed and, in the final section, some of the most important directions for future research will be outlined.

2. Temperature dependence of the grain boundary free energy

The grain boundary free energy of a pure material is expected to decrease linearly with increasing temperature because of the entropic term in the free energy. Measurements of pure Ni and Cu, among other materials, are consistent with this expectation [8–10]. For example, in the temperature range between 600 and 1000 °C, the grain boundary energy of Cu decreases by 0.4 J/m^2 and in the temperature range between 800 and 1400 °C, the grain boundary energy of Ni decreases by 0.1 J/m^2 [9]. Atomistic simulations can be used to calculate the temperature dependence of the grain boundary energy and these results also show that the energy decreases with temperature [11–16]. However, the decrease in energy is not perfectly linear, especially at temperatures near absolute zero and close to the melting point [13]. Over this range, Foiles [13] determined that the grain boundary energy of Ni decreases from 1.2 J/m^2 at 0 K to 0.4 J/m^2 at the melting point. For comparison, the surface energy of Cu decreases about 25% from room temperature to the melting point [12]. The evidence from both the experiments and the calculations suggest that the decrease in the grain boundary energy of pure materials is continuous.

In a system with impurities or alloying components, the situation is expected to be different. In most cases, the solute will accumulate at the grain boundaries and reduce the grain boundary energy. As temperature increases, the bulk solubility usually increases; if the solute from the intergranular regions dissolves in the bulk, the boundary excess will be reduced, and this will increase the grain boundary free energy. This general idea has been

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used to interpret a large amount of alloy data that shows grain boundary energies increase with temperature. For example, the grain boundary energies of Cu alloys with ⩽1 atomic percent Zr, Te, Ti, or Cr increases by 0.035 J/m^2 (Zr) to 0.065 J/m^2 (Cr) between 700 and 900 °C [8,9]. Measurements of Ga–Pb alloys have shown that surfaces behave in a similar way, with the surface energy increasing as the surface excess decreases at higher temperatures [17]. In other words, the increases in grain boundary energy driven by the change in boundary composition more than compensate for the entropic factor that tends to reduce the grain boundary energy. Changes in the grain boundary energy that occur because of the de-segregation of solute from the boundaries at high temperature are thought to be continuous, at least until the solute is depleted and the entropic effect prevails.

If the solute content of a boundary is metastable, and it transitions to a stable composition, then there can be a discontinuous change in the grain boundary composition and this might lead to a discontinuous change in energy. For example, in yttria doped alumina, it has been observed that increases in Y content (or decreases in the total grain boundary area from grain growth) lead to increased grain boundary excess of Y [18]. The grain boundary excess reaches a maximum of 9 Y/nm^2 and then, at higher concentrations, yttrium aluminum garnet (YAG) precipitates form and the grain boundary excess decreases to a value that remains constant (6–7 Y/nm^2) with an increased concentration of Y. This decrease in Y excess at the boundaries would presumably lead to an abrupt increase in the grain boundary energy. If a Y-doped alumina ceramic supersaturated in Y is heated, then at the temperature that YAG precipitates, one might also expect an abrupt lowering of the grain boundary excess and a corresponding increase in the grain boundary energy.

Precipitation of a second phase is one mechanism that can occur to partition excess solute in the microstructure, but it is now known that transitions to thicker grain boundary complexions (carrying more solute) are also possible. If, as temperature changes, one grain boundary complexion becomes more stable than another, then the rate of change of the grain boundary energy with temperature will also change (see Fig. 1(d)) [7,19,20]. If the boundary remains in a metastable state at a higher temperature, then, when the boundary ultimately transforms, there will be a discontinuous change in the energy. Phase boundaries likely behave in a similar way, and it has been shown that the formation of an interface complexion at a gold-sapphire interface reduces the interface energy [3].

The four possible scenarios for the change in the grain boundary energy with temperature, at constant bulk composition, are illustrated in Fig. 1. Note that they lead to characteristic differences in the temperature dependence; continuous negative (a) or positive (b) slopes indicate that the temperature dependence is driven by entopic effects or impurity de-segregation, respectively. Both of these cases have been observed experimentally [9]. An abrupt increase in grain boundary energy, as illustrated in Fig. 1(c), is expected to occur if precipitates form and the boundaries are depleted of solute. To the author's knowledge, no reports illustrating this effect on the grain boundary energy have been reported. If there is a complexion transition, then the temperature dependence of the grain boundary energy will change slope [7,19,20]. If the transition must be activated, and the higher energy complexion exists in a metastable state until sufficiently super heated, then there will be an abrupt decrease in the grain boundary energy, as indicated in Fig. 1(d). These characteristically different phenomena make it possible to distinguish between precipitation and a complexion transition and this is the basis for some of the experiments described Section 4 [21–27].

3. Grain boundary energy measurements

Experimental grain boundary energy measurements are usually carried out by observing the geometry of interface junctions assumed to be in thermodynamic equilibrium [28]. In this context, we will consider grain boundary thermal grooves that form when a

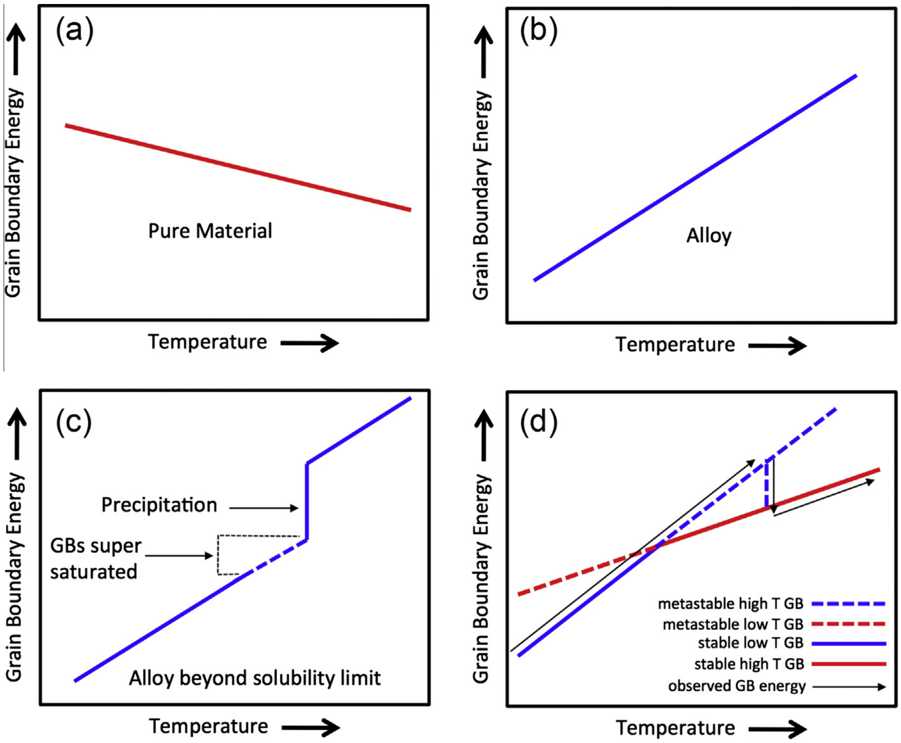

Fig. 1. Schematic depictions of how the average grain boundary energy can vary with temperature in (a) a pure material, (b) an alloy with segregating solute, (c) an alloy where the solubility limit is exceeded, and (d) a material with multiple grain boundary complexions.