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Complexion time-temperature-transformation (TTT) diagrams: Opportunities and challenges

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ABSTRACT

Grain boundaries and other interfaces can undergo complexion transitions from one thermodynamic state to another, resulting in discontinuous changes in interface properties such as diffusivity, mobility, and cohesive strength. The kinetics of such complexion transitions has been largely overlooked until recently. Just as with bulk phase transformations, complexion transition kinetics can be represented on time-temperature-transformation (TTT) diagrams. An experimental complexion TTT diagram is presented here for polycrystalline Eu-doped spinel annealed at 1400–1800 °C. This material developed a microstructure with a bimodal grain size distribution, indicating that a complexion transition occurs within this temperature range. The time and temperature dependence of this complexion transition was analyzed and used to produce a grain-boundary complexion TTT diagram for this system. Complexion TTT diagrams have the potential to be remarkably useful tools for manipulating the properties of internal interfaces in polycrystalline metals and ceramics. The development of experimental complexion TTT diagrams is likely to have an important impact on the field of grain-boundary engineering, and hence the development of these experimental diagrams should be an intense area of focus in the coming years.

1. Introduction

Davenport and Bain made a pivotal breakthrough in our understanding of bulk phase kinetics when they introduced the first experimental time-temperature-transformation (TTT) diagrams in 1930, which were based on a detailed and extensive study of steel phase transformation kinetics [1]. These TTT diagrams were revolutionary because they offered a simple and easily understood visual representation of a complicated and often mysterious process. The power and utility of TTT diagrams was immediately recognized, and the subsequent widespread usage of these diagrams enabled rapid progress in the processing and heat treatment of steel and other alloys.

Interfaces such as grain boundaries can also exhibit phase-like behavior [2], transforming from one equilibrium state to another as a function of thermodynamic variables in a process known as a complexion transition [3]. Complexion transitions are important because they are often accompanied by discontinuous changes in grain-boundary properties such as mobility, diffusivity, and cohesive strength, and hence these transitions can dramatically influence the macroscopic properties of materials [3]. Although the study of complexion transitions dates back decades, as summarized in recent review articles [3,4], the kinetics of complexion transitions has been largely overlooked by the materials community until very recently. Just as with bulk phase transformations, complexion transitions take time to occur, and therefore their kinetics can be represented on TTT-style diagrams. The first experimental complexion TTT diagrams were recently reported based on grain growth studies of polycrystalline Y_2O_3 and Al_2O_3 [5]. These diagrams clearly show the combinations of time and temperature at which grain-boundary complexion transitions occur, unifying and displaying a large data set in a readily understood format.

Although grain-boundary complexion TTT diagrams are analogous to bulk phase TTT diagrams in many ways, there are important differences between them. For example, bulk phase TTT diagrams typically only show the transformation curve for the cooling transformation which, in its simplest form, is described by a C-shaped transformation band (see Fig. 1(a)) that results from a competition between nucleation and growth rates. This

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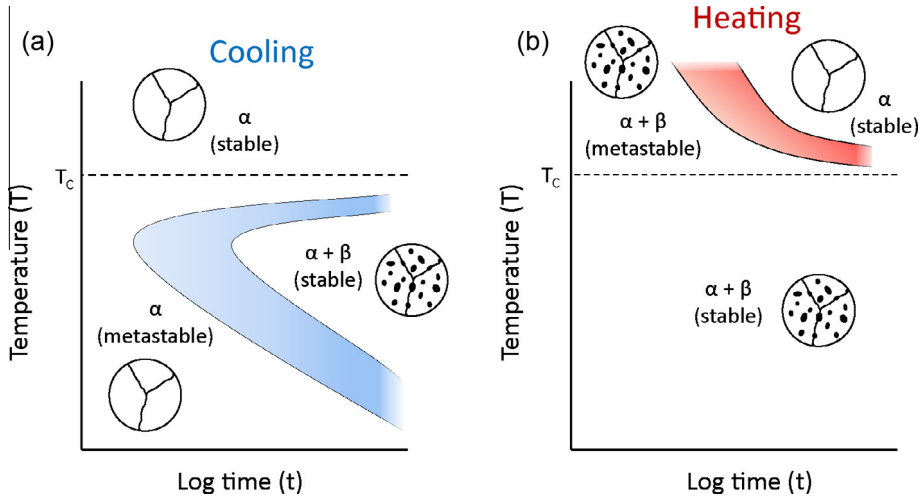

Fig. 1. Schematic bulk phase TTT diagrams for a hypothetical system that transitions between a single α phase and α + β phases as a function of temperature: (a) Isothermal cooling and (b) isothermal heating.

competition produces a minimum transformation time at a particular sub-cooling temperature, often referred to as the nose of the TTT curve. On the other hand, during the heating transition, the nucleation and growth rates both increase as temperature increases and hence augment each other, leading to a transformation that occurs ever more rapidly with increasing temperature. A heating transition diagram therefore lacks the classic nose feature of the cooling diagrams. An isothermal heating transformation is shown schematically in Fig. 1(b). Although cooling TTT diagrams are typically most useful for bulk phases due to their importance in heat treatment operations, heating TTT diagrams are arguably more important for the study of grain-boundary complexion transitions. If the heat treatment temperature exceeds the complexion transition temperature, discontinuous jumps in the grain-boundary diffusivity and mobility can lead to runaway grain growth (e.g., during sintering), enhanced oxidation rates, and other potentially undesirable effects. Thus, by understanding the temperature *and time* limits within which grain-boundary complexion transitions will *not* occur, enhanced protocols for materials processing under various service conditions can be developed.

It is apparent from Fig. 1 that the regions of bulk phase metastability are reversed for cooling and heating TTT diagrams. In the TTT cooling diagram in Fig. 1(a), the α phase is metastable *below* T_C for short times, whereas in the TTT heating diagram in Fig. 1(b), the α + β microstructure is metastable *above* T_C for short times. Complexion TTT diagrams exhibit analogous regions of metastability [5], suggesting that they undergo nucleation and growth processes similar to those characteristic of bulk phases. One signature of a grain-boundary complexion transition is the appearance of abnormally large grains [3,6], and experiments have shown that the number density of abnormal grains increases exponentially with temperature [7], an observation that is consistent with a nucleation and growth mechanism. Although no direct evidence exists yet that grain-boundary complexion transitions occur via a nucleation and growth process, it has been shown experimentally that surface complexion transitions do involve nucleation and growth processes [8]. It therefore seems reasonable that an analogous nucleation and growth process occurs during grain-boundary complexion transitions, although more research is needed in this area to elucidate the true behavior.

Another fundamental difference between bulk phase TTT diagrams and grain-boundary complexion TTT diagrams is that grain boundaries have five additional degrees of thermodynamic freedom as compared to bulk phases, i.e. the five macroscopic parameters that describe grain misorientation and grain-boundary inclination (three parameters for grain misorientation, and two for grain-boundary plane inclination). Complexion transition kinetics can vary from one grain boundary to another because grain boundaries of different character exist in different thermodynamic states owing to difference in interfacial atomic geometry. It has been shown that complexion transitions preferentially occur on higher energy interfaces [9] at shorter annealing times than transitions on lower energy interfaces [5]. Therefore, the grain-boundary character distribution (GBCD) and the resultant grain-boundary energy anisotropy present in a polycrystalline material may lead to grain-boundary complexion transitions occurring at a variety of different times and temperatures. For example, within a given polycrystalline specimen, some high energy grain boundaries might undergo a complexion transition at relatively low temperatures and short times, while other grain boundaries with lower energies might not transition until higher temperatures and longer times. Furthermore the lowest energy grain boundaries might not undergo a complexion transition prior to melting. This variety of kinetic behavior caused by the structural and energetic anisotropy of grain boundaries means that a complexion TTT diagram should, in principle, contain a different transformation band for each type of grain boundary. This situation is shown schematically for two grain boundaries of different character in the isothermal heating complexion TTT diagram in Fig. 2.

Of course, a complexion TTT diagram that contains a transformation curve for each different type of grain boundary in a polycrystalline material would be incredibly complex and would therefore have limited utility. In practical cases, a subset of grain boundaries will undergo a complexion transition under similar conditions [3]. Therefore, it will often be preferable to group together subsets of grain boundaries with similar behavior when plotting grain-boundary complexion TTT diagrams, such that each subset has its own transformation curve.

Grain-boundary complexion TTT diagrams are advantageous for depicting the kinetics of complexion transitions because they illustrate, in a readily understood format, the complex relationship between annealing time, temperature, and properties that depend on these transitions. Hence, one can imagine that complexion TTT diagrams will be useful, for example, for controlling grain size during annealing and sintering, and will have additional applications in other situations in which complexion transitions play a key role. The ability to understand and control the kinetics of complexion transitions will be critical to advancing the state of the art in