Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 62 (2014) 1–48
Acta MATERIALIA
www.elsevier.com/locate/actamat

Overview No. 152

Grain boundary complexions

Patrick R. Cantwell [a], Ming Tang [b,1], Shen J. Dillon [c], Jian Luo [d], Gregory S. Rohrer [e], Martin P. Harmer [a,*]

[a] Department of Materials Science and Engineering, Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, PA 18015, USA
[b] Condensed Matter and Materials Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA
[c] Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, IL 61801, USA
[d] Department of NanoEngineering, Program of Materials Science and Engineering, University of California, San Diego, La Jolla, CA 92093-0448, USA
[e] Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

Received 3 May 2013; received in revised form 20 July 2013; accepted 22 July 2013
Available online 4 September 2013

Abstract

Grain boundaries exhibit phase-like behavior in which their structure, chemistry and properties may change discontinuously at critical values of thermodynamic parameters such as temperature, pressure and chemical potential. Therefore, grain boundaries (and other interfaces such as surfaces and heterophase boundaries) can be treated as thermodynamically stable interfacial states. To differentiate these interfacial states from bulk phases, the term “complexion” has been introduced. A variety of terminology has been used to describe complexions and complexion transitions. In many cases, several terms exist that describe essentially the same phenomenon. We give an overview of complexion-related terminology, suggest a preferred nomenclature and discuss a classification framework that can be used to categorize complexions and complexion transitions. The field of grain boundary complexions has evolved rapidly in the past decade due to advances in experimental equipment – in particular, aberration-corrected transmission electron microscopy – and progress in computational simulation methods. Grain boundary complexion transitions are the root cause of a wide variety of materials phenomena – such as abnormal grain growth, grain boundary embrittlement and activated sintering – that have defied mechanistic explanation for years. In this overview, we review the history and theory of grain boundary complexion transitions, their role in materials processing and their effect on materials properties.

Keywords: Grain boundary; Complexions; Phases; Transitions; Kinetics

1. Introduction

Grain boundaries strongly influence the properties and behavior of polycrystalline materials during processing and in service [1]. Grain boundary energy, mobility, diffusivity, cohesive strength and sliding resistance – all of which depend upon local structure and chemistry – determine bulk materials behavior and properties such as superplasticity, creep, fatigue, corrosion, strength and conductivity [2]. Grain boundary specialists have long recognized that grain boundaries can be considered as quasi-two-dimensional “phases” that may undergo phase-like transitions in which their structure and chemistry changes abruptly at critical values of thermodynamic parameters [1,3–11]. As predicted by Hart [5], the grain boundary properties most strongly affected by these transitions will be the non-equilibrium properties, such as mobility, diffusivity, intergranular cohesive strength and grain boundary sliding resistance. Equilibrium grain boundary properties, such as energy, specific volume and adsorption, will also be affected, but in general are less accessible to experiment than non-equilibrium grain boundary properties. If a significant fraction of the grain boundaries in a polycrystalline material undergo a transition, the cumulative effect can be a dramatic and rather sudden change in macroscopic properties [5].

---

* Corresponding author. Tel.: +1 610 758 4227.
E-mail address: mph2@lehigh.edu (M.P. Harmer).

[1] Present address: Shell Technology Center, Houston, TX 77082, USA.

1359-6454/$36.00 © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.actamat.2013.07.037

Grain boundary complexion transitions have traditionally been called grain boundary "phase transitions", in analogy to bulk phase transitions. Interfaces such as grain boundaries can be analyzed using equilibrium thermodynamics [12] and may transform in a manner analogous to bulk phase transitions, but equilibrium interfacial states do not satisfy the Gibbs definition of a phase because they are inhomogeneous and may have gradients of structure, composition, properties and other order parameters. Therefore, Tang et al. [13] introduced the term "complexion"[2] to denote an equilibrium interfacial state. A complexion, concisely defined, is interfacial material or strata that is in thermodynamic equilibrium with the abutting phase(s) and has a stable, finite thickness that is typically on the order of 0.2–2 nm [14]. A complexion cannot exist independently of the abutting phases and its average composition and structure need not be the same as the abutting phases.

com·plex·ion ***noun*** **\kəm-ˈplek-shən**
Interfacial material or strata that is in thermodynamic equilibrium with its abutting phase(s)

The term "complexion" has been adopted by the authors of this overview [11,15–36], and has been recognized [37–41] and adopted [42–45] by others. Therefore, in this overview the term "grain boundary complexion" will be used rather than "grain boundary phase" to describe an equilibrium grain boundary state, even though the original "phase" terminology may have been used by the original author(s). Similarly, although the "surface phase" terminology is widely used in the surface science community, equilibrium interfacial states at free surfaces will be referred to here as "surface complexions".

Grain boundary complexion transitions are difficult to predict a priori and typically occur independently of bulk phase transformations, i.e. at different values of temperature, pressure or composition. Therefore, they often result in unexpected and seemingly inexplicable phenomena. In 1968, Hart postulated that grain boundary complexion transitions could be responsible for temper embrittlement in steel [3–5], although he recognized that insufficient experimental evidence existed at the time to support the hypothesis [4]. It was not until 20 years after Hart's first paper that the existence of grain boundary complexion transitions was deemed to be conclusive [8]. Since then, advances in transmission electron microscopy and other experimental techniques have provided strong evidence that grain boundary complexion transitions are responsible for materials phenomena as diverse as abnormal grain growth [17,46], solid-state activated sintering [47] and liquid–metal embrittlement [48].

Interfaces can be separated into two groups: external interfaces (e.g. surfaces) and internal interfaces (e.g. grain boundaries, heterophase boundaries, stacking faults and antiphase boundaries) [9]. All of these interfaces play an important role in materials science, and understanding their phase-like behavior has been identified as one of eight grand challenges in ceramic science [49]. In this overview, we will focus on grain boundary complexions and their impact on materials properties and processing. We will also occasionally discuss surface complexions and heterophase boundary complexions when appropriate to illustrate important concepts.

2. The fundamentals of grain boundary complexions

Seminal articles on the fundamentals of grain boundary transitions include those by Hart [3,5], Cahn [6] and Rottman [8,9]. Grain boundary transitions are also discussed in the textbook on crystalline interfaces by Sutton and Balluffi [1]. In this section, we will summarize the main points and conclusions of these thermodynamic treatments.

While the vast majority of research on grain boundary complexions has focused on non-pure systems in which grain boundary segregation plays a critical role, grain boundary complexion transitions may occur in even pure materials. We will first discuss grain boundary complexions in pure materials to illustrate their fundamental characteristics. Then we will discuss the more complicated complexion transitions in non-pure systems that can involve changes in grain boundary composition as well as structure.

2.1. Thermodynamic parameters of grain boundaries

The fundamental thermodynamic quantity that characterizes grain boundaries (and interfaces in general) is the energy per unit area, γ, which represents the amount of work required to create one unit of grain boundary area via a reversible process. In other words, γ represents the additional (excess) free energy per unit area that exists in the system due to the presence of the grain boundary. The value of γ is a function of both bulk and interfacial thermodynamic parameters. The usual bulk thermodynamic parameters are temperature (T), pressure (P) and/or chemical potential (μ_i) (or, alternatively, composition [6]). There are five interfacial thermodynamic parameters that describe the five macroscopic degrees of freedom of a grain boundary. Several different geometric conventions exist for describing these five parameters [50]. For ease of conceptual understanding, we use the simple convention followed by Rottman [9], in which three variables specify the misorientation vector $\boldsymbol{R}$ between the two crystals and two independent variables in the form of a unit vector, $\hat{\boldsymbol{n}}$, specify the average orientation of the grain boundary plane normal (i.e. the grain boundary plane inclination). The misorientation vector $\boldsymbol{R}$ is defined by a rotation of angle ω around a direction common to both grains specified by a unit vector $\hat{\boldsymbol{u}}$, i.e. $\boldsymbol{R} = \hat{\boldsymbol{u}}\omega$. Given a misorientation vector $\boldsymbol{R}$, the rotation angle and axis can be recovered using the relations $\omega = |\boldsymbol{R}|$ and $\hat{\boldsymbol{u}} = \boldsymbol{R}/\omega$.

The energy of a grain boundary defined using these parameters depends upon $6 + C$ independent variables,

---

[2] The term "complexion" was tentatively suggested by W.C. Carter and embraced by R.M. Cannon.