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Rapid solidification of non-stoichiometric intermetallic compounds: Modeling and experimental verification

Jianbao Zhang [a], Haifeng Wang [a, *], Wangwang Kuang [a], Yachan Zhang [a], Shu Li [b], Yuhong Zhao [c, *], D.M. Herlach [d, *]

[a] *State Key Laboratory of Solidification Processing, Center of Advanced Lubrication and Seal Materials, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China*
[b] *College of Applied Science, Harbin University of Science and Technology, Harbin, Heilongjiang 150080, PR China*
[c] *School of Materials Science and Engineering, North University of China, Taiyuan 030051, PR China*
[d] *Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft-und Raumfahrt (DLR), 51170 Köln, Germany*

ABSTRACT

The thermodynamic extremal principle was applied to model of rapid solidification of non-stoichiometric intermetallic compounds and the Co-$x$at.%Si alloys ($x = 50$, 53, 55) were undercooled to test the model. It is the model with but not the model without solute drag that can be derived self-consistently in thermodynamics. Unique dual sluggish and abrupt growth stages were found in under-cooled Co-53 at.%Si and Co-55 at.%Si alloys. The first (second) sluggish stage is solute-controlled (thermal-controlled). The first (second) abrupt growth stage is ascribed to the sharp occurrence of solute trapping (inverted partitioning) and disorder trapping that initiates the transition from solute-controlled (thermal-controlled) to thermal-controlled (kinetic-controlled) growth. Since the predictions by the current (previous) model with (without) solute drag predicted well (deviate drastically from) the experimental results, solute drag was suggested be significant upon rapid solidification. The current work solved such an open problem, i.e. solute drag in solidification, and is helpful for not only understanding the non-equilibrium phenomena that is of theoretical importance but also controlling the non-equilibrium microstructures that is of technological importance.

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1. Introduction

Ascribing particularly to their potential use as high-temperature structure-materials [1–3], intermetallic compounds have been studied extensively. Their low ductility and brittle fracture at room temperature however limit greatly their practical applications. Such a problem could be solved by rapid solidification, e.g., the refined and/or metastable microstructures can improve substantially their ductility and fabricability [4]. Furthermore, interaction of migrating interface and solute atoms upon rapid solidification may result in several non-equilibrium phenomena [5]. Compared with the solid-solution alloys with solute trapping and solute drag, the non-stoichiometric compounds with different kinds of sub-lattices exhibit several unique characteristics [6], e.g. disorder trapping, inverted partitioning etc. Modeling of rapid solidification of non-stoichiometric intermetallic compounds therefore is of significance for not only controlling the non-equilibrium micro-structures that is of technological importance but also under-standing the non-equilibrium phenomena that is of theoretical importance.

The classical work for modeling of disorder trapping and solute trapping was carried out by Boettinger and Aziz [7]. The solid phase was assumed to be consisted of two equivalent sub-lattices but without vacancies; see Fig. 1a. Solidification was treated to be a superposition of two distinct reactions [8,9], i.e. crystallization via advance of the interface across a monolayer of liquid alloy (i.e. interface migration [5]) and solute-solvent redistribution via inter-diffusion of solute atoms between the liquid and solid monolayers (i.e. trans-interface diffusion [5]). The rate of each reaction was determined individually by the chemical rate theory, in which the corresponding driving force should be given in advance.

* Corresponding authors. State Key Laboratory of Solidification Processing, Center of Advanced Lubrication and Seal Materials, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China.
E-mail addresses: haifengw81@nwpu.edu.cn (H. Wang), haifengw81@nwpu.edu.cn, zhaoyuhong@nuc.edu.cn (Y. Zhao), haifengw81@nwpu.edu.cn, Dieter.Herlach@dlr.de (D.M. Herlach).
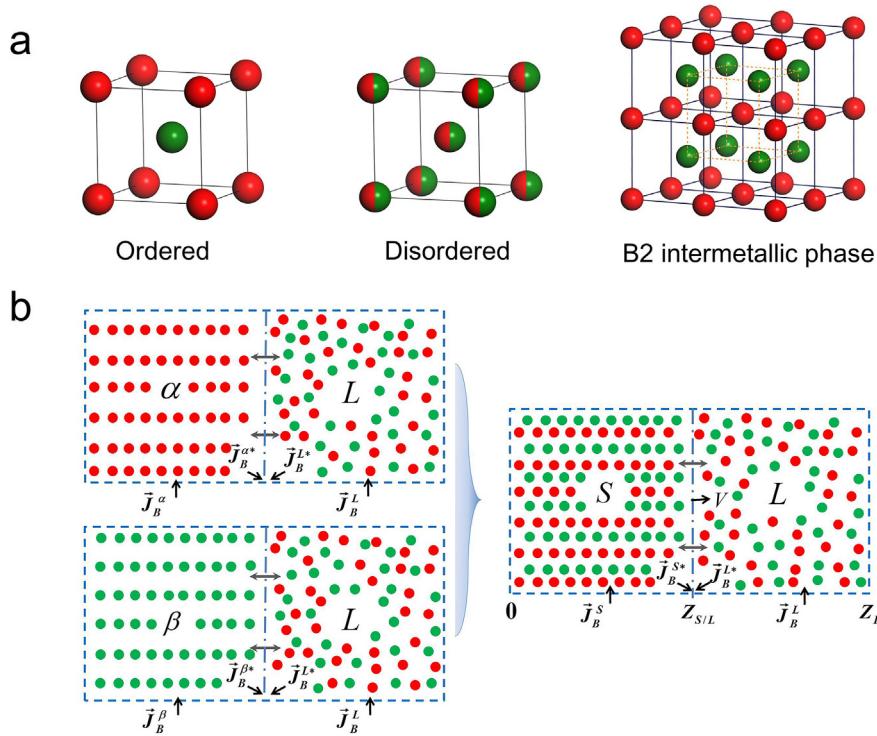
Fig. 1. (a) Schematic crystal structures of ordered solid, disordered solid and B2 intermetallic compound with two equivalent sub-lattices but without vacancies. The long range order parameter η, i.e. the difference between the molar fractions of solute B in the two sub-lattices, is one for a perfectly ordered solid but zero for a disordered solid. (b) Schematic diagram for planar solidification of a non-stoichiometric compound with two equivalent sub-lattices (α and β) but without vacancies. In the solid, there are two dissipation processes (i.e. solute diffusion in the α and β sub-lattices) and $J_B^S = \frac{1}{2}(J_B^\alpha + J_B^\beta)$. In the liquid, there is one dissipation process, i.e. solute diffusion in the liquid with the diffusion flux as J_B^L. At the S/L interface, solute diffusion from the solid to the interface with the diffusion flux as J_B^{S*}, solute diffusion from the interface to the liquid with the solute diffusion flux as J_B^{L*} and interface migration with the crystallization flux as J_C are constrained by the mass conservation law Eq. (5), i.e. $J_B^{S*} - J_B^{L*} = J_C(C_S^* - C_L^*)$. The S/L interface can be divided into two sub-interfaces, i.e. the α/L and β/L interfaces where the mass conservation laws $J_B^{\alpha*} - J_B^{L*} - J_C(y_B^{\alpha*} - C_L^*) = 0$ and $J_B^{\beta*} - J_B^{L*} - J_C(y_B^{\beta*} - C_L^*) = 0$ hold. In this sense, the dissipation processes in the solid (at the interface) can be taken to be summation of solute diffusion in the α and β sub-lattices (tans-interface diffusion and interface migration at the α/L and β/L interface).

Consequently, three governing equations were derived for interface migration, trans-interface diffusion between one sub-lattice and the liquid, and trans-interface diffusion between the other sub-lattice and the liquid (see Fig. 1b), according to which the interface velocity, the interface temperature, the long-range order-parameter, the molar fractions of solute in the two sub-lattices and the liquid at the interface can be obtained uniquely. The model was extended subsequently to the case in which the solid phase possesses two non-equivalent sub-lattices but still without vacancies (e.g. Ni₃Al) [10]. Such models [7,10] are able to predict a progression from solidification of a solid phase with equilibrium long-range order-parameter and equilibrium partition coefficient to solidification of a disordered solid phase with the same molar fraction as the liquid, i.e. complete disorder trapping and solute trapping.

The above work on modeling of rapid solidification of non-stoichiometric intermetallic compounds [7,10] belongs to the model without solute drag, whereas in the initial work of Aziz and Kaplan [8,9] on rapid solidification of solid-solution alloys, both the model with and without solute drag were proposed. After a comparative study between the model predictions and the experimental results in rapid solidification of Si-As alloys, solute drag was found to be absence in solidification [11,12]. After integrating the interface kinetic model of Aziz and Kaplan [8,9] into the dendrite growth model of Boettinger et al. [13], absence of solute drag was also found in undercooled Ni-B alloys but the possibility of partial solute-drag in rapid solidification cannot be eliminated absolutely [14,15]. In contrast, presence of solute drag in solid-state phase-transformations has been widely proved by experiments and

well adopted by modeling [5,16], following which the model with solute drag was also adopted to rapid solidification of solid-solution alloys [17,18]. As for rapid solidification of non-stoichiometric intermetallic compounds, even though dendrite growth of B2 intermetallic compound in undercooled Ni-50 at.%Al [19], Ni-40.3 at.%Al and Ni-47.1 at.% Al [20] alloys was well predicted by the model without solute drag [7], the B2 intermetallic compound with two equivalent sub-lattices and vacancies [21–23] was re-assessed arbitrarily in thermodynamics to neglect vacancies [24]. In other words, solute drag in rapid solidification is still an open problem.

Recently, the thermodynamic extremal principle (TEP) [25,26] has been developed to be a handy tool for modeling of complex thermodynamic systems with complex additional constraints. It has been applied so far to diffusion and creep [27], precipitation [28], diffusion-controlled phase-transformation [29,30], grain growth and coarsening [31] etc. In contrast to the chemical rate theory, the dissipation processes and their corresponding driving free energies are determined by the derivation process itself and do not need to be given previously anymore. Application of the TEP to rapid solidification of solid-solution alloys [32,33] shows that only the model with solute drag can be derived self-consistently in thermodynamics. Further application to rapid solidification of Si-As alloys indicates that the conclusion of Kittl et al. [11,12], i.e. absence of solute drag in solidification, is actually based on their unreasonable description of the Si-As phase-diagram. If the recent reassessment of Si-As alloy system [34] was adopted, the effect of solute drag becomes significant in solidification [32], being consistent to the fact that solidification and solid-state phase