A metallic glass composite: Phase-field simulations and experimental analysis of microstructure evolution

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Abstract

The growth process of a crystalline dendritic solid phase from an undercooled melt in the metallic glass composite Zr−Ti−Nb−Ni−Cu−Be is analyzed by experimental investigations and by adaptive finite element simulations based on a multicomponent phase-field model. The phase transition: L(liquid) → S(dendrite) + M(matrix) can be described by considering a pseudo-ternary system of late transition metals A = (Zr, Ti, Nb), of early transition metals B = (Ni, Cu) and of the component C = (Be). Scanning and transmission electron microscopy are employed to experimentally determine structural properties of the two-phase system and to provide concentration distributions of the components across the dendrite/matrix interface. The computed and experimentally observed microstructures, length scales and chemical compositions are in good agreement.

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1. Introduction

Multicomponent systems, such as e.g. technical metal alloys or bulk metallic glass (BMG) matrix composites [1–3] represent a new important class of materials that has promised relevant technological and industrial applications. The possible implementations of these materials are numerous ranging from mechanical to magnetic. They have therefore evoked the interest of many research groups which have been characterizing these systems trying to link their physical properties to the structural ones (e.g. [1,4]). Mechanical and magnetic properties of BMG composites have been shown to depend strongly on their structural features [4,5], and understanding the crystallization mechanisms that determine microstructure formation is thus of fundamental importance. For instance, the crystallization process in these systems involves the diffusion and interdiffusion of multiple components and is, in general, accompanied by the appearance of multiple phases and different types of phase transitions. The properties of the crystallized phases depend sig-

nificantly on the composition of the system. Hence, materials with defined properties can, in principle, be tuned by varying the chemical composition and by adjusting suitable crystallization conditions. However, due to the complexity of the systems, their systematical and quantitative study by means of experimental analysis, modelling and numerical simulation remains a challenging task and is therefore restricted to a small number of multicomponent systems. In fact, modelling the coupled transport phenomena requires the input of several parameters as thermodynamical data (e.g. latent heats and melting temperatures), surface energies, and anisotropies, diffusion and interdiffusion coefficients.

In this paper, we investigate the solidification of a dendritic phase from an undercooled melt in a six-component Zr−Ti−Nb−Ni−Cu−Be metallic glass composite by experiments and by phase-field simulations. The experimentally observed microstructures as well as the concentration distributions are compared with the results obtained from adaptive finite element simulations. To perform the numerical computations of the dynamic process of dendritic growth, we apply a recently formulated phase-field approach (see Ref. [6] for details) that has been set up to model mass and heat transport in non-isothermal multicomponent, multiphase systems. The phase-field model is

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configured to incorporate the physical data of the metallic glass composite. We consider a pseudo-ternary approximation of the six-component system as proposed by experimental observations.

The use of a phase-field model has the computational advantage of avoiding the explicit tracking of a sharp interface profile at the solid–liquid phase boundary related with the free boundary problem of crystal growth by introducing a smooth phase-field variable $\phi(\vec{x}, t)$ with a diffuse interfacial layer at the solid–liquid interface. In our model formulation, the variable ϕ takes the value $\phi = 1$ and $\phi = 0$ in the bulk solid and in the bulk liquid phase, respectively. In the interfacial region, $\phi(\vec{x}, t)$ varies smoothly in the interval $0 \leq \phi \leq 1$ over a finite thickness ϵ. In fact, the origin of formulating a phase-field model goes back to early works by [7]. Since then, the concept has continuously been developed with increasing interest over the last 15 years due to the broad range of prospects with respect to computational applications. Diffuse interface approaches have been applied to a variety of phenomena such as crystal growth, grain growth, solid–liquid and solid–solid phase transitions, pure substances and alloys, electrochemical reactions, crack formation, nucleation, elasticity and fluid flow (see e.g. [8–15] and references therein). Instead of giving an extensive review and commenting on each direction of application in detail, we refer to a review article in Ref. [16]. Phase-field models related to multiphase ($\geq$three phases) and/or multicomponent ($\geq$two components) systems are described in Refs. [11,13,14,17]. Since crystal growth involves complex surface geometries, different length and time scales, multiple components and phases, various physical fields, the computation requires the development of efficient numerical methods with respect to computing time and memory resources. Within the last 5 years, hybrid algorithms, adaptive finite element methods as well as parallel solving schemes have been reported [18–20]. Due to the strongly localized profiles of the field variables in the neighborhood of the interfaces, adaptive methods are particularly suitable for solving phase-field equations since they allow high resolution in regions of strong gradients.

In Sections 2 and 3, we describe the experimental characterization of as-prepared $Zr_{56}Ti_{14}Nb_5Cu_7Ni_6Be_{12}$ samples and the phase-field equations for the adaptive finite element simulations. The comparison between experimental and simulated microstructures and chemical compositions is shown in Section 4, and we draw conclusions in Section 5.

2. Experimental results

Samples of the multicomponent alloy $Zr_{56}Ti_{14}Nb_5-Cu_7Ni_6Be_{12}$ referred to in this work were produced by cooling the homogeneous melt slightly above its critical cooling rate. Nucleation and dendritic growth of a crystalline phase followed by solidification of the remaining liquid alloy are the mechanisms responsible for the complex microstructure of the specimens consisting of Zr-rich dendrites embedded in a remnant amorphous matrix [21]. As-prepared samples were characterized to determine the structure and the chemical composition of the two-phase system by the use of X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning elec-
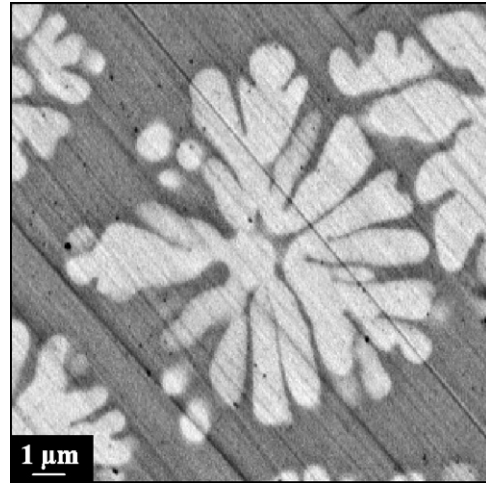

Fig. 1. Backscattered-electron SEM image of the as-quenched $Zr_{56}Ti_{14}-Nb_5Cu_7Ni_6Be_{12}$ alloy confirming the composite nature of the samples. The dendrites (bright areas) are embedded in a remnant amorphous matrix (dark area).

tron microscopy (SEM), and high-resolution transmission electron microscopy (HTEM) with energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS). In Fig. 1, a SEM image recorded by detecting backscattered electrons arising from a polished surface of $Zr_{56}Ti_{14}Nb_5Cu_7Ni_6Be_{12}$ specimen is presented.

The image confirms the composite nature of the sample which shows dendritic structures (bright areas) grown with a characteristic length scale of a few μm embedded in a remnant matrix (dark area) of different chemical composition. X-ray diffraction and selected area electron diffraction have shown that the dendrites have a body-centered cubic (bcc) structure while the matrix is fully amorphous [21]. The crystalline precipitates are the result of a primary crystallization involving nucleation-and-growth of the dendrites and atomic diffusion mechanisms in the interdendritic regions. The resultant concentration differences between dendrites and matrix have been determined qualitatively by energy-filtered HTEM (EFTEM) and quantitatively by EDX analysis.

Fig. 2 shows EFTEM images recorded on a $Zr_{56}Ti_{14}-Nb_5Cu_7Ni_6Be_{12}$ sample at the Cu and Zr energy-loss edge, respectively. The contrast differences across the dendrite/matrix interface are clearly an indication of differences in the concentration of the two elements.

Analogous measurements taken at the Be energy-loss value have furthermore shown that the dendrites are Be-depleted with a EFTEM signal below the experimental detection limit of the technique. On the contrary, the matrix results to be enriched in Be, Cu, and Ni but slightly depleted in Zr, as the differences in contrast in Fig. 2b also suggest. From EFTEM and EDX analyses, it can be concluded that the chemical composition of the dendrites is $Zr_{70}Ti_{15}Nb_9Cu_4Ni_2$, while that of the Be-rich matrix is $Zr_{49}Ti_{13}Nb_3Cu_9Ni_8Be_{18}$ [21].

These results allow to treat the complex multicomponent $Zr_{56}Ti_{14}Nb_5Cu_7Ni_6Be_{12}$ alloy like a pseudo-ternary system introducing the pseudo components A = (Zr, Ti, Nb) of the early transition metals, B = (Ni, Cu) of the late transi-