



Rapid solidification morphologies in Ni₃Ge: Spherulites, dendrites and dense-branched fractal structures



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ABSTRACT

Single-phase β -Ni₃Ge has been rapidly solidified via drop-tube processing. At low cooling rates (850–300 μm diameter particles, 700–2800 K s^{-1}) the dominant solidification morphology, revealed after etching, is that of isolated spherulites in an otherwise featureless matrix. At higher cooling rates (300–75 μm diameter particles, 2800–25,000 K s^{-1}) the dominant solidification morphology is that of dendrites, again imbedded within a featureless matrix. As the cooling rate increases towards the higher end of this range the dendrites display non-orthogonal side-branching and tip splitting. At the highest cooling rates studied (<75 μm diameter particles, >25,000 K s^{-1}), dense-branched fractal structures are observed. Selected area diffraction analysis in the TEM reveals the spherulites and dendrites are a disordered variant of β -Ni₃Ge, whilst the featureless matrix is the ordered variant of the same compound. We postulate that the spherulites and dendrites are the rapid solidification morphology and that the ordered, featureless matrix grew more slowly post-recrystallization. Spherulites are most likely the result of kinetically limited growth, switching to thermal dendrites as the growth velocity increases. It is extremely uncommon to observe such a wide range of morphologies as a function of cooling rate in a single material.

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1. Introduction

Chemically ordered intermetallic compounds have attracted considerable interest due to their potential application as high temperature structural materials resulting from their good chemical stability and high hardness at elevated temperatures. However, poor room temperature ductility limits their formability which has restricted industrial uptake of these materials. One route to increasing low temperature ductility is rapid solidification processing, wherein rapid crystallization results in a reduction of the degree of chemical ordering. Reordering of the material immediately following crystallization results in fine pattern of antiphase domains (APD's) which gives rise to increased ductility [1–3]. Importantly, the high temperature properties of the intermetallic can be restored by chemical ordering via annealing out the APD's subsequent to forming [1]. As such, understanding the process of disorder trapping and the morphology of the disordered regions following rapid solidification processing is critical to the increased

uptake of intermetallics in high temperature structural applications.

APD's result from the transformation of the disordered solid to the ordered form via a nucleation process, with atom locations within a given nucleus being sublattice specific such that ordering between neighbouring nuclei is different [4]. Moreover, the morphology of the APD's formed during rapid solidification depends heavily upon the cooling rate of the solid following growth [5]. For modest cooling rates columnar APD's are formed. At higher cooling rates equiaxed APD's can be formed while at very high cooling rates all reordering is suppressed.

For a given system we can define a critical temperature, T_c , at which the free energies of the ordered and disordered solid phases are equal. For the case in which $T_c/T_M < 1$ (with T_M being the melting temperature) equilibrium growth of the solid will initially occur in the disordered state, with a subsequent disorder-order transformation occurring in the solid-state as the temperature drops below T_c . Conversely, if $T_c/T_M > 1$, equilibrium growth to the ordered solid phase will occur directly from the liquid. It is in such cases that rapid solidification can result in disordered growth as a consequence of the high growth rate, a phenomenon termed disorder trapping. Disorder trapping may be considered analogous to

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the more familiar process of solute trapping, wherein a non-equilibrium solute distribution occurs at the solid-liquid interface due to rapid solidification [6]. The extent of disorder trapping may be measured via the Long-Range Order (LRO) parameter, η , where $\eta = 1$ represents the fully ordered intermetallic and $\eta = 0$ is a random solid-solution.

In studying the effect of disorder trapping within intermetallics, congruently melting compounds are particularly attractive as, even during equilibrium solidification, a melt at the correct stoichiometry for the compound will solidify without partitioning. Disorder trapping may therefore be studied without the complication of considering simultaneous solute trapping. For such a congruently melting compound η will decrease with increasing solidification velocity as progressively higher levels of chemical disorder are trapped in the structure [7]. In a second order transition η falls continuously with increasing growth velocity, approaching zero at sufficiently high velocity. Conversely, in a first order transition, η decreases continuously from its equilibrium value, until a critical velocity, V_C , is reached, above which η drops discontinuously to zero.

It has been demonstrated in a range of intermetallic systems (see e.g. Ref. [8] in relation to the B2 AlNi phase, and [9] in relation to CoSi) that growth of the ordered phase is significantly slower than that of the disordered phase, with a jump in the growth velocity being evident at the (1st order) disorder-order transition. In a previous paper Ahmed et al. [10] studied disorder trapping in the congruently melting compound β -Ni₃Ge using a flux undercooling technique. Unlike most other ordered intermetallics that have been subject to rapid solidification studies, β -Ni₃Ge shares the L1₂ crystal structure with the important high temperature materials Ni₃Al and Ti₃Al. A maximum undercooling of 362 K was observed for β -Ni₃Ge, wherein the corresponding growth velocity was measured at 3.55 m s⁻¹. In common with other researchers who have determined the velocity-undercooling curves for intermetallic compounds passing through the order-disorder transformation [10], observed a discontinuous break in the curve at the onset of fully disordered growth. This condition was observed for β -Ni₃Ge at an undercooling of 168 K and at a critical growth velocity of 0.22 m s⁻¹. This compares with $V_C = 0.75$ m s⁻¹ in Fe-18 at.% Ge [11] and $V_C = 3.8$ m s⁻¹ in CoSi [9]. Microstructural analysis of the β -Ni₃Ge system [10] revealed a transition from a coarse grained structure during ordered growth to a much finer grained structure once disordered growth was achieved. However, post-recalence cooling is very slow in flux undercooling experiments (~10 K s⁻¹), meaning that any microstructural evidence of disorder trapping will have been extensively modified in the as-solidified sample, with no prospect of observing either APD's or retained disordered material.

Other closely related intermetallic systems include Fe₃Ge and β -Ni₃Si. Fe₃Ge has an ordered hexagonal D0₁₉ structure and so cannot be considered directly analogous to β -Ni₃Ge. It forms via the peritectic reaction $L + \alpha_2 \rightarrow \epsilon$, where α_2 is an ordered B2 phase, although for undercoolings in excess of 140 K direct solidification to the ϵ phase should be possible. However, no evidence of an order-disorder transformation was observed at undercoolings up to 198 K, wherein the growth velocity was measured at 1.3 m s⁻¹. Conversely, one of the three β -Ni₃Si polymorphs does have the ordered fcc L1₂ crystal structure. However, while the phase diagram suggests single phase growth of β -Ni₃Si from the Ni-25 at.% Si melt should be possible for undercoolings in excess of 43 K, both flux undercooling [12] and drop-tube studies [13] have revealed that such direct growth of β from the melt appears to be inhibited at all undercoolings in favour of a α Ni- γ eutectic, γ being the phase Ni₃Si₁₂.

In this article we present an analysis of rapidly solidified Ni-23.8 at.% Ge produced using the drop-tube technique. Depending

upon particle size, cooling rates in the drop-tube vary from 700 to 50,000 K s⁻¹, giving much greater scope than the work of [10] to retain disorder trapping and APD's in the as-solidified microstructure. As such the main objective of this work is to study the morphology of any retained regions of the disordered solid together with that of any APD's formed during post-recalence reordering in a single-phase system that acts as a simple model for high temperature L1₂ intermetallics.

2. Experimental method

According to the phase diagram of Nash and Nash [14], the Ni-rich portion of which is shown in Fig. 1, β -Ni₃Ge is a congruently melting compound with a melting point of 1405 K. It has a homogeneity range of 22.5–25 at.% Ge and crystallizes to the ordered fcc L1₂ structure.

Elemental Ni and Ge were obtained from Alfa Aesar with purity of 99.99% and 99.999%, metals basis, respectively. The alloy, of composition Ni-23.8 at.% Ge, was produced by arc-melting the elemental constituents together under a protective argon atmosphere at a pressure of 5×10^{-4} Pa before back-filling with argon gas to a pressure of 3.4×10^3 Pa. A 230 A arc was produced using a tungsten electrode. The material was melted by manipulating the electrode above the sample, a process that was repeated 8 times to ensure uniform mixing of the final alloy. The final alloy was weighed following arc-melting to ensure there was no loss of material.

Following arc-melting the alloy ingot was sectioned using a Struers Accutom diamond precision saw and its phase composition checked using a PANalytical Xpert Pro X-ray diffractometer (XRD). The sectioned ingot was then mounted in transoptic resin using a Buehler Simplotter 1000 Automatic mounting press before being ground using progressively finer Silicon carbide grinding paper. The sample was then prepared for microstructural analysis by polishing with 6 μ m, 3 μ m and 1 μ m diamond paste, with the sample being washed and dried between each polishing step. The sample was then etched using Nital before being subject to microstructural analysis using an Olympus BX51 optical microscopy (OM) and a Carl Zeiss EVO MA15 scanning electron microscopy (SEM) equipped

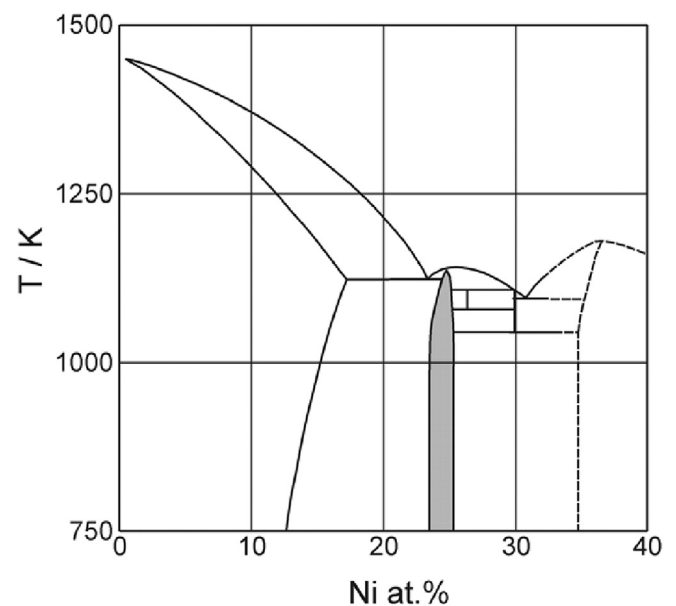


Fig. 1. Ni-rich portion of the Ni-Ge phase diagram (based upon that of [14]), with the β -Ni₃Ge phase shown shaded.

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