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Non-equilibrium solidification of intermetallic compounds in the Ni-Al alloy system

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Abstract

Ni-Al alloy system exhibits particular solidification behavior due to chemical long-range order of the intermetallic compounds Ni_3Al ($L1_2$) and NiAl (B2). Using rapid solidification technique their slow solidification kinetics leads to the entrapment of solute atoms and/or disorder, respectively. In the present work containerless processing by applying electromagnetic levitation technique is used to analyze the aspects of dendrite growth, as observed in solidification of undercooled Ni-Al melts. Sharp-interface modeling is used to illustrate the effect of chemical order on the solidification kinetics of intermetallic phases. Both experimental results and theoretical work denote the role of chemical order in solidification of Ni-Al intermetallics.

Introduction

Binary Ni-Al alloys which include a chemically ordered intermetallic phase are of special interest because of their importance in both theoretical study and practical applications. The relevant properties for technological applications of intermetallic compounds NiAl (β-phase) and Ni_3Al (γ'-phase) are high melting temperature, comparatively low mass density, good oxidation resistance and high intrinsic yield stress [1]. However, the ductility of them is quite limited but can be improved by means of rapid solidification processes. The kinetics of rapid solidification of the chemically ordered intermetallics can be remarkably different from that of disordered solid solutions, resulting in substantial interfacial undercoolings or invertible partitioning [2]. The Ni-rich side of the Ni-Al alloy system has been studied in detail with respect to deviations from chemical equilibrium at the solidification front causing disorder trapping leading to a drastic decrease of the chemical order of the superlattice structure [3, 4]. During subsequent cooling to room temperature, the atoms tend to diffuse and to reorder on different sublattices. This solid state transformation leads to the formation of antiphase domain patterns which has been found to increase the ductility of compounds.

Chemical order in Ni-Al alloy melts plays an important role for the formation of phases and microstructures during solidification. In particular, the high degree of chemical order of the β-phase (NiAl) and γ'-phase (Ni_3Al) requires a massive diffusion process during crystallization. In addition to the previous work [5] dendritic growth velocity of the intermetallic β- and γ'-phases is measured for an $Ni_{75}Al_{25}$ alloy melt at different undercooling levels. Modeling of crystal growth of an intermetallic ordered phase is developed based on the sharp interface model which takes into account both solute trapping and disorder trapping. The model predictions are compared with the experimental data on solidification of the $Ni_{75}Al_{25}$ alloy melt.

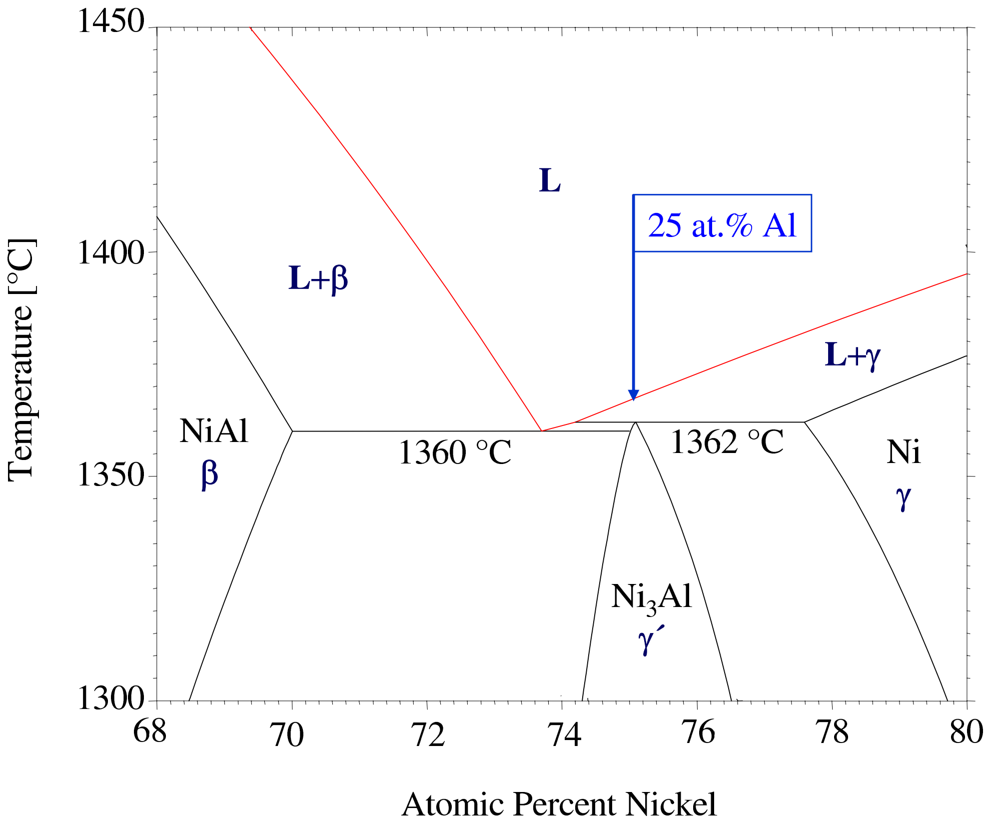

Figure 1: Phase diagram "temperature - concentration" for a NiAl alloy in a region of concentration investigated.

Experimental

Alloy with composition of $Ni_{75}Al_{25}$ is prepared by arc-melting high purity elemental materials (Ni 99.99 % and Al 99.9999 %) under the protection of an argon atmosphere (99.999 % purity). Before levitation under terrestrial conditions, an alloy sample of about 1 g is placed onto a hollow quartz sample holder and positioned in the levitation coil in an electromagnetic levitation facility, of which relevant details can be found elsewhere [5]. After evacuation to a pressure in the order of 10^{-6} mbar, the chamber of the levitation facility is backfilled with highly purified helium gas (99.9999 %) to a pressure of about 500 mbar. The alloy sample is then levitated and melted under this pressure. In order to attain a substantial undercooling, the sample is shortly overheated to a temperature of 100 K to 200 K above liquidus temperature. Subsequently, the sample is cooled by blowing helium gas onto the sample surface. After reaching a certain undercooling, the sample solidifies either spontaneously or triggered by the touch of the trigger needle. The sample temperature before and during solidification is measured using a two-color pyrometer with a relative accuracy of ± 5 K and recorded using a transient recorder. The bulk undercooling of the sample is determined from the measured temperature-time profile as difference between the liquidus temperature of the sample and the onset temperature of the first recalescence effect. In addition, the solidification process is observed by a high-speed camera (Photron Fastcam Ultima APX) at a frequency of up 120,000 frames per second depending on the desired resolution. The high frequency of the video camera allows for the detection of the advancing growth front which is characterized by the difference in emissivity of the undercooled liquid (dark) as-solidified material (bright) as already introduced before [5]. The growth process can be described by steady-state dendritic growth where the growth front is depicted by the intersection of the envelope of all dendrites with the sample surface [6]. All samples are processed in the same way.

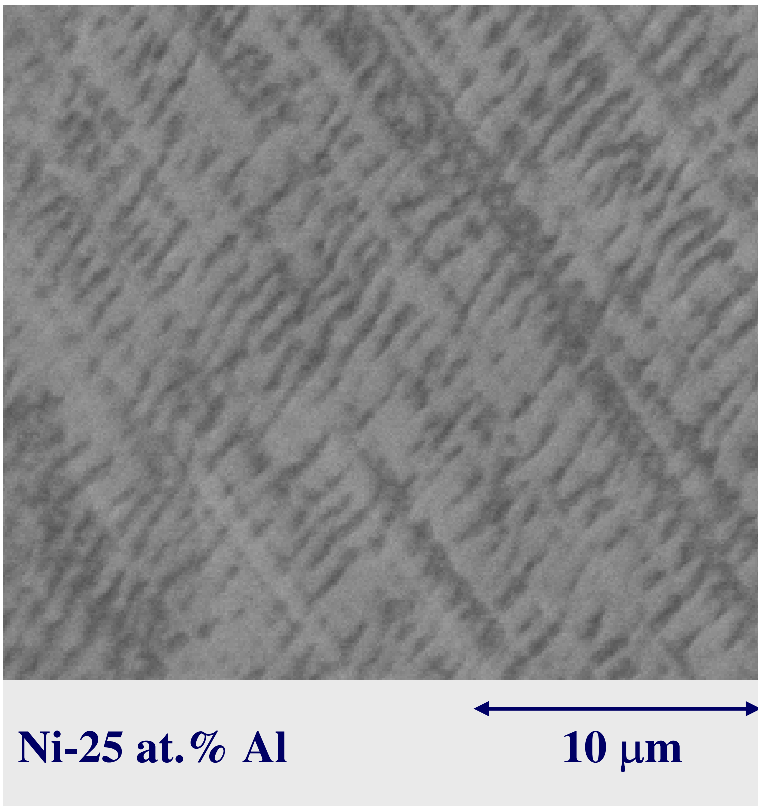

Figure 2: Scanning electron microscope (SEM) picture of the dendritic pattern as-solidified $Ni_{75}Al_{25}$ alloy. Initial undercooling is $\Delta T = 50$ K.

The as-solidified samples are retrieved for subsequent microstructural investigations. The microstructures are examined with an LEO1530VP scanning electron microscope (SEM) under back scattering conditions. Elemental concentrations of phase constituents and of the bulk samples are analyzed using an energy dispersive X-ray micro-analyzer (EDX) fitted to the SEM. In addition, X-ray diffraction (XRD) analyses of the samples are performed with Fe-K_α radiation.

Results and discussion

Experimental results

A part of the Ni-Al alloy's equilibrium phase diagram in a region of investigated concentration is shown in Fig. 1. For different undercoolings relatively equilibrium liquidus of the $Ni_{75}Al_{25}$ alloy, nonequilibrium crystal growth has been measured as relationship "growth velocity vs. undercooling". It has been found that the crystals were growing with a dendritic form as is shown in Fig. 2.

Kinetic data "dendrite growth velocity vs. undercooling" for the intermetallic β- and γ'-phase are depicted in Fig. 3 for $Ni_{75}Al_{25}$ alloy's composition. Electromagnetic levitation processing, equipped with a high-speed camera system, is used to melt, undercool and monitor solidification of melts [6]. Through careful analysis of camera images, crystal growth velocity is worked out, with reasonable high accuracy, as a function of composition, and undercooling level prior to solidification. Fig. 3 shows a comparison between experimental

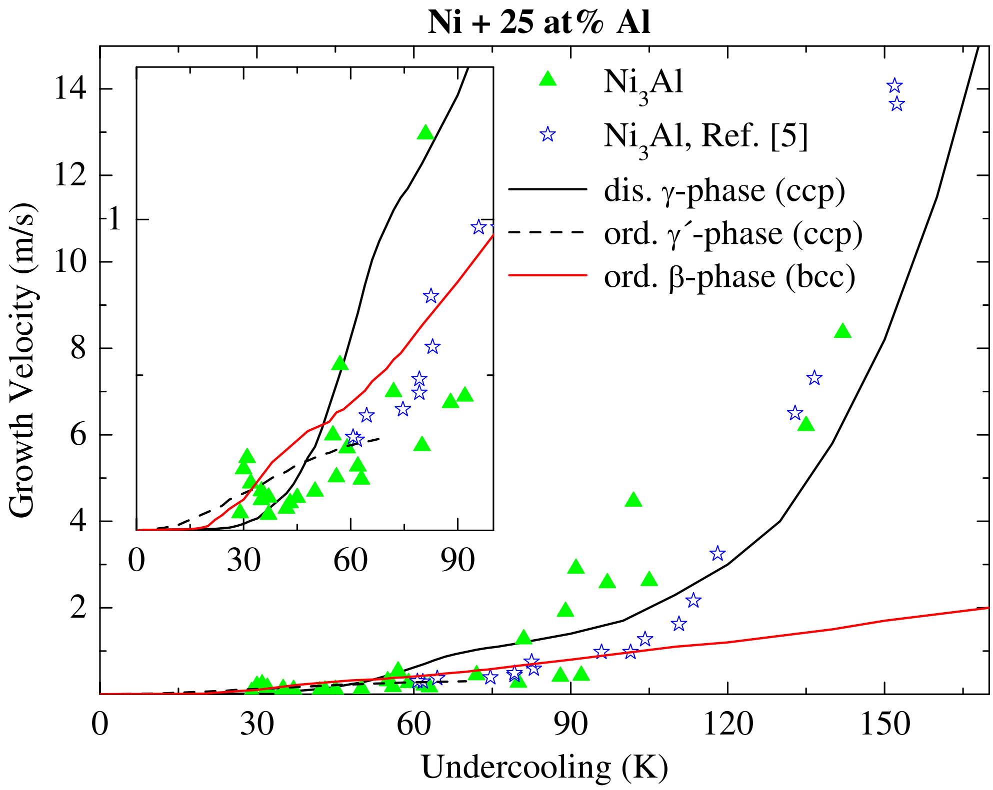

Figure 3: Dendrite growth velocity as a function of undercooling in $Ni_{75}Al_{25}$ alloy as it has been measured previously (stars, Ref.[5]) and currently (triangles).

data for growth of ordered β-phase (data points up to approx. 90 K of undercooling) and for growth of disordered γ-phase (data points approx. above 110 K of undercooling).

Within a region of $\approx$ 90...110 K of undercooling a gradual transition from ordered growth of β-phase to disordered growth of γ-phase is clearly visible. It is confirmed by present measurements: increasing of the dendrite growth velocity occurs for $\approx$90...110 K of undercooling (see filled triangles in Fig. 3). Note that, in the present work, growth of disordered β-phase was not detected and reached by undercooling. For higher undercooling one can find growth of disordered β-phase for the $Ni_{75}Al_{25}$ alloy as it has been shown in Ref. [4].

Theoretical predictions

For the theoretical predictions of the dendrite growth velocity, we assumed that solidification of intermetallic alloy proceeds with disorder trapping. Following Boettinger and Aziz [7], the solid crystal phase has been divided in two sublattices which are responsible for solute trapping of the undesirable species on each sublattice. Order parameter is evaluated as a difference for the atomic concentration between sublattices. Thermodynamic computations were made using the Gibbs free energy for β and γ phases. Using these computations, kinetic phase boundaries are calculated for various growth velocity of a planar interface. Finally, dendrite growth velocity is calculated as a function of the initial (base) undercooling. This procedure is described in Ref. [4].

The model predictions in comparison with experimental data described in a previous subsection are shown in Fig. 3. From this comparison, it is seen that the growth of β-dendrites may occur up to 110 K of undercooling. However, a transition "order-disorder" begins to proceed from 60 K of undercooling and growth of the ordered β-dendrites changes to growth of the disordered γ-dendrites. The transition is clearly visible in the inset of Fig.

3. Moreover, detailed analysis of this transition leads to conclusion that, in addition to growth of the ordered β-dendrites, the ordered γ'-dendrites may grow as well in the region of small undercoolings (see inset in Fig. 3). Therefore, one can conclude that the transition to disordered growth of γ-phase may occur from both ordered β-dendrites and ordered γ'-dendrites.

Conclusions

1. Solidification of $Ni_{75}Al_{25}$ alloy melts was investigated in small droplets processed by electromagnetic levitation technique.
2. Microstructure analysis has shown that the growth of crystals in $Ni_{75}Al_{25}$ alloy is predominantly dendritic.
3. Dendritic growth velocity has been measured as a function of the initial (base) undercooling in a range of $30 - 150$ K.
4. The model predictions and experimental data exhibit a transition from the ordered β-dendrites to the growth of the disordered γ-dendrites. Detailed analysis of this transition leads to conclusion that the transition to disordered growth of γ-phase may occur from both ordered β-dendrites and ordered γ'-dendrites.

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