Dendritic solidification in undercooled Ni–Zr–Al melts: Experiments and modeling

P.K. Galenko [a,*], S. Reutzel [a], D.M. Herlach [a], S.G. Fries [b,d], I. Steinbach [b], M. Apel [c]

[a] *Institut für Materialsphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), D-51170 Köln, Germany*
[b] *ICAMS, Ruhr-Universität Bochum, Stiepeler Strasse 129, D-44780 Bochum, Germany*
[c] *ACCESS eV, Intzestrasse 5, D-52072 Aachen, Germany*
[d] *SGF Scientific Consultancy, Arndtstr 9, D-52064 Aachen, Germany*

Abstract

The kinetics of dendritic solidification in a ternary $Ni_{98}Zr_1Al_1$ alloy is investigated experimentally in a range of melt undercoolings $40\,K \leqslant \Delta T \leqslant 320\,K$. The growth velocity is measured for samples processed by the electromagnetic levitation technique using a high-speed video camera. With $\Delta T \lesssim 220\,K$ the measured growth rates are the same as those of a binary $Ni_{99}Zr_1$ alloy. In the regime of rapid solidification, especially within the regime of thermal dendritic growth at $\Delta T \gtrsim 220\,K$, growth rates are decreased. Sharp-interface modeling predicts growth rates over the whole range of undercooling. Phase-field simulations give quantitative predictions for the dendritic growth velocity in the solute-controlled growth regime. Results show that the composition and temperature dependency of the thermodynamic data, e.g. liquidus slope and solute partition coefficient, are important for describing the alloys. Our findings give improved sharp-interface model predictions compared to calculations based on an approximation of the thermodynamic data derived from binary phase diagrams.

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1. Introduction

The solidification of undercooled Ni–Zr alloys has been investigated previously at dilute compositions with small amounts of Zr. The first measurements of dendritic growth velocities V were obtained as a function of the undercooling ΔT in levitated droplets of Ni–Zr alloys using the electromagnetic levitation technique [1,2]. Recent progress in experimental measurements and a theoretical description of dendritic growth and of fragmentation in Ni–Zr alloys are described in Refs. [3,4]. In particular, it has been found experimentally that small, controlled amounts of Zr in Ni, of the order of 0.1 at.% Zr and smaller, enhance the dendrite growth velocity in comparison with "nominally pure"

Ni. In addition, forced convection in small droplets may play an essential role in the formation of a dendritic microstructure. These effects were found and explained for a range of low and moderate undercoolings. For high undercoolings, theoretical predictions were in reasonable agreement with experimental data, showing an abrupt change in the growth kinetics with a break point in both the "velocity–undercooling" relationship and the "tip radius–undercooling" relationship. This break point occurs at a critical undercooling and solidification velocity for the onset of the diffusionless growth of crystals. An overview of these explanations is given in Ref. [5].

Even though the dendritic growth velocity is reasonably well predicted over the whole range of undercoolings for the dilute Ni–Zr alloys, it has been shown in Ref. [6] that the theoretical curve overestimates the experimental data in the region of diffusion-limited growth with $\Delta T < 90\,K$. One reason for this disagreement could be the dependence

* Corresponding author. Fax: +49 (02203) 601 2255.
  E-mail address: Peter.Galenko@dlr.de (P.K. Galenko).

of the solute partitioning k_e and the liquidus slope m_e on the temperature and composition of the multicomponent alloy. In previous modeling, both parameters were considered constant.

In the present paper, we analyze the growth of dendrites in the $Ni_{98}Zr_1Al_1$ alloy. First, we compare new results on dendrite growth velocities extracted from a high-speed-camera system with previously obtained experimental data on solidification of the $Ni_{99}Zr_1$ alloy. Secondly, the predictions of a sharp-interface model are compared with experimental data on both $Ni_{98}Zr_1Al_1$ and $Ni_{99}Zr_1$ alloys over the whole range of undercooling investigated. Thirdly, we investigate solidification microstructures using numerical methods and compare the predictions of a phase-field model with those of a sharp-interface model in the range of solute diffusion-limited growth.

2. Experimental procedures

2.1. Sample preparation

The experiments for detecting dendritic growth velocities of Ni–Zr–Al alloy melts were carried out using an electromagnetic levitation facility as described elsewhere (see Ref. [5] and references therein). Ni–Zr–Al alloys were prepared by arc-melting high-purity elemental materials (Ni of 99.99%, Zr of 99.99%, and Al of 99.999%) under the protection of an argon atmosphere (99.999% purity). Each alloy sample of about 6–8 mm in diameter—depending on the respective composition and mass of the sample—was inserted into the levitation coil in the ultra-high vacuum (UHV) chamber and held using an alumina sample holder. The chamber was evacuated to a pressure of 10^{-7} mbar and refilled to 10^3 mbar using an inert gas atmosphere (He) of 99.9999% purity. Afterwards, the alloy sample was levitated under this pressure. In order to attain a substantial undercooling, the sample was briefly overheated to a temperature of 100–200 K above its liquidus temperature. The sample was then cooled by blowing the inert gas onto the sample surface. After reaching a certain undercooling, the sample solidified spontaneously and was retrieved for subsequent metallographic characterization and thermal analysis.

2.2. Growth velocity measurements

The sample temperature before and during solidification was measured using a two-color pyrometer with a relative accuracy of 5 K, and recorded using a transient recorder. In addition, the solidification process was observed by a high-speed camera (Photron Fastcam Ultima APX) at a frequency of up to 120,000 frames per second (fps) 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 and the as-solidified material. The growth process can be described by steady-state dendritic growth where the growth front is depicted by the inter-

section of the envelope of all dendrites with the sample surface. The combination of the high-speed camera technique with the detection of the moving solid–liquid interface at the sample's surface as recently described by Assadi et al. [7] allows for a reasonably accurate evaluation of dendrite growth velocities in spontaneously solidified samples.

2.3. Measurements of liquidus temperatures

Differential thermal analysis was used to verify the transition temperatures of the solidified samples. Previously electromagnetically processed alloy samples solidified at different supercooling levels were measured by a differential heat flow calorimeter (Netzsch DSC 404) using non-metallic crucibles (Al_2O_3). The ceramic crucibles were encapsulated into platinum pans to avoid excessive heat exchange by radiation and to enhance the reproducibility of the high-temperature measurements [8]. Calibration runs with pure metals Cu, Ni and Au yielded an absolute accuracy in temperature of +2 K compared to literature values [9]. Ni-Zr-Al alloy samples were first heated and then cooled at rates of 5–10 K min^{-1} under a flowing Ar atmosphere.

3. Experimental results: Dendritic growth velocities

Experimental data for the dendrite growth velocities as a function of the melt undercooling for the alloys $Ni_{99}Zr_1$ and $Ni_{98}Zr_1Al_1$ are presented in Fig. 1. No significant difference between the two alloys could be observed with respect to the dendrite growth velocities in the range of undercooling of $40 < \Delta T(K) < 175$. The fact that both alloys show the same behavior can be attributed to the weak segregation of Al in this regime. For a melt undercooling of $\Delta T > 175$ K, the data for the dendrite velocity obtained during solidification of the two alloys disagree (Fig. 1). This occurs when solute trapping comes into action and the solidification velocity suddenly increases beyond $\Delta T \approx 175$ K. Therefore, one can conclude that Al affects behavior in the high-undercooling region: it may decreases the solute trapping effect for Zr in the $Ni_{98}Zr_1Al_1$ alloy or add an additional contribution to the solutal undercooling, leading to a lower solidification velocity in comparison with the $Ni_{99}Zr_1$ alloy.

4. Material parameters

4.1. Gibbs energy database

For the calculation of the thermodynamic properties we use the Ni–Al–Zr Gibbs energy database given in Ref. [10]. This databases, which was constructed using the CALPHAD method [11], allow for calculation of liquidus and solidus slopes, enthalpies of formation, heat capacities, chemical potentials, thermodynamic factors, etc., at stable and metastable states. For the present calculations, we use ThermoCalc [12] as it also provides the library of routines (TQ interface) used for the driving force calculations in the phase-field code MICRESS [13,14].