Metastable solidification in undercooled liquid droplets of Fe-Ni based soft-magnetic alloys under terrestrial and microgravity conditions

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Abstract. Microstructure evolution and metastable phase formation in undercooled melts of Fe-Ni based soft magnetic alloys were studied by the electromagnetic levitation technique in ground-based experiments and under microgravity during parabolic flight campaigns. Discontinuous changes in the microstructure were observed in samples of a commercial soft magnetic alloy quenched at distinct melt undercooling $\Delta T$. The results were successfully interpreted within the framework of the dendrite breakup model. No metastable phase formation was detected in commercial soft magnetic alloys which possess higher Ni contents. Under microgravity conditions the lifetime of the metastable bcc phase formed for Fe$_{90}$Ni$_{10}$ beyond a critical melt undercooling increases. The surface tension of the levitating droplets under microgravity was determined from high speed video recordings of the oscillations of the droplets. The value obtained, $\sigma = 1.90 \pm 0.01$ Nm$^{-1}$, agrees well with values from the literature.

1. Introduction

Commercial, soft magnetic, Fe-Ni based alloys are normally Ni-rich compositions which also contain various trace elements [1, 2]. The solidification behaviour of these materials at sizeable melt undercooling has rarely been studied. Better understanding of microstructure evolution can contribute to the optimisation of production routes of soft magnetic materials. Dramatic changes in the microstructure of samples processed by electromagnetic levitation (EML) and quenched at given melt undercooling ($\Delta T$) have been reported [3]. Similar discontinuous changes in the grain size at critical $\Delta T$ have also been observed in the binary alloys Cu-Ni [4], Ni-Zr [5]. Generally, at low $\Delta T$, a grain refined microstructure is observed, at intermediate $\Delta T$, a coarse grained structure is present and at higher $\Delta T$, a return to the refined grains is seen. The critical values of $\Delta T$ which define the boundaries between these transitions are known as $\Delta T^*_1$ and $\Delta T^*_2$. A recent theory, developed by Karma et al. [4, 6] is that partial remelting and breakup of the dendrites during recalescence is responsible for the grain refinement. The results from the commercial Fe-Ni alloys were successfully interpreted in terms of
this dendrite breakup model by considering the multicomponent compositions as ternary Fe-Ni-C systems [3].

The effect of convective fluid flow on microstructural transitions resulting in grain refinement via instabilities of growing dendrites has been recently theoretically analyzed [7]. Microgravity experiments enable the study of microstructural transitions in undercooled melts under conditions where this gravity-driven convection is reduced by one order of magnitude. Changes of the critical undercoolings of the microstructural transitions, $\Delta T_1^*$ and $\Delta T_2^*$, are expected during these microgravity experiments [8]. Microgravity can be achieved for a short time ($\sim 20$ s) during parabolic flights. In this time scale, melt undercoolings up to $\Delta T \sim 100$ K are accessible and the results can be used to justify the theoretical predictions concerning the first microstructural transition (i.e. up to and including $\Delta T_1^*$). Longer duration of microgravity, available in the TEMPUS electromagnetic levitation facility on the International Space Station (ISS), is required in order to access the whole range of melt undercooling ($> 200$ K) necessary to explore these microstructure phenomena fully.

In the Fe-Ni binary system, the primary solidification switches from b.c.c. $\delta$-Fe to the f.c.c. $\gamma$-(Fe,Ni) phase at a Ni fraction $> 5$ at.%. Beyond this concentration (up to 17 at.% Ni) the $\delta$-Fe can also solidify as metastable phase if a critical melt undercooling $\Delta T_c$ is exceeded [9]. This is concluded from the occurrence of double-recalescence events, which reflect the primary solidification of the metastable phase and its subsequent decomposition into the equilibrium phase after a limited lifetime. These experiments provide an unique opportunity to measure the solidus of metastable phases. Such results from EML experiments with Fe-Co alloys have been used to provide input for computer optimisation of the Fe-Co phase diagram [10].

EML experiments in microgravity conditions, with Fe-Co for example, have indicated important differences in the behaviour of the metastable phase compared to terrestrial experiments. The $\Delta T_c$ is reduced and the arrest time before the transformation to the equilibrium phase is prolonged because of the reduced fluid flow in the levitated droplet under microgravity [11, 7].

The aim of the present work was to compare the solidification processes in undercooled melts of binary Fe-Ni alloys and commercial Fe-Ni based soft magnetic materials in EML experiments under terrestrial and microgravity conditions. The focus is on possible metastable phase formation and the variation of microstructure as function of undercooling prior to solidification.

2. Experimental methods

Ingots of Fe$_{90}$Ni$_{10}$ were prepared from Fe and Ni elements with 4N purity in a Hukin-type cold-crucible melting facility under Ar atmosphere. A commercial Fe-Ni based soft magnetic material (P36) was provided by ThyssenKrupp VDM GmbH. The nominal composition of the alloy is given elsewhere [2, 3]. The materials were sectioned into pieces of approximately 1 g mass in order to give an optimum droplet size for EML of $\sim 6$ mm. In ground-based EML experiments the apparatus detailed by Löser et al. [12] was used. For details of the experimental parameters used for the commercial material, refer to [3].

Undercooling experiments under microgravity conditions were carried out during parabolic flight campaigns with the TEMPUS EML facility. Temperature-time profiles were recorded from a high-speed photo diode. A high speed video camera was installed in the facility and videos showing the behaviour of the droplets during the levitation experiments were recorded at 10 kHz. The videos allowed the morphology of the solidification front to be observed in detail and the surface tension of the liquid droplets to be measured. The undercooling phase was used for the surface tension measurements. Measurements were recorded over 200 K with a mean temperature of 1583 K. An edge detection algorithm was used to extract the dimensions of the droplet along two different axes as a function of time. Oscillations of the droplet dimensions due to its liquid nature occurred and the frequency of these is proportional to the surface tension. The measurements were therefore transformed into the Fourier domain and the sum or difference of the resulting peaks was extracted for the surface tension calculation. This procedure was carried out using the software TeVi 3.41 of S.E.A. Datentechnik GmbH and DLR-MUSC, Linder Höhe, 51147 Köln, Germany.
3. Growth kinetics and grain coarsening of commercial Fe-Ni based soft-magnetic alloys

Terrestrial EML experiments were used to achieve melt undercoolings of $\Delta T > 320$ K in a commercially available Fe-Ni based soft magnetic alloy (P36). Temperature profiles, recorded from the photo diode, showing the recalescence during solidification of this alloy at various values of $\Delta T$ are shown in figure 1. The temperature profiles become steeper with increasing $\Delta T$, indicating higher solidification speed. A simple linear approximation was used to estimate the solidification front speed from the temperature profiles. The values shown in figure 2 are a lower limit because the surface of the spherical droplet is projected onto the diode and thus the signal measured does not take into account the curvature of the droplet. The estimated front speed increases monotonically with $\Delta T$ and at the highest values of $\Delta T$ reaches 30 ms$^{-1}$, meaning that solidification is complete within $\sim 0.1$ milliseconds.

Figure 1. Recalescence curves for the Fe-Ni based alloy P36 (34 at% Ni). The solidus temperature is shown as a dotted line.

Figure 2. Front speed vs. melt undercooling $\Delta T$ evaluated from the recalescence curves of the alloy P36.

Undercooling of $\Delta T = 327$ K represents highly non-equilibrium solidification conditions but in spite of this, there is no double-recalescence behaviour, indicating that no metastable phase forms. The reason for this is the high Ni content (34 at.%) of this alloy. Solidification of the f.c.c. $\gamma$-(Fe,Ni) phase occurs because nucleation of the metastable b.c.c. $\delta$-Fe phase is thermodynamically unfavourable, even at such extreme melt undercoolings.

The figure 3 shows optical micrographs of the commercial Fe-Ni based alloy quenched at various values of $\Delta T$. The range of $\Delta T$ is larger than has been shown in previous microstructural investigations [3]. Microstructural transitions are apparent which can be interpreted using the Karma model [6]. At $\Delta T = 0$ K, a microstructure of refined equiaxed grains superimposed on a substructure of spherical elements was observed. Here $\Delta T < \Delta T_1^*$ and therefore $t_{bu} < t_{pl}$ ($t_{bu}$ = dendrite breakup time; $t_{pl}$ = plateau time during which the sample temperature is above the solidus due to recalescence). Thus remelting and breakup of the primary crystals occurred leading to the refined microstructure. At $\Delta T = 81$ and 135 K, the microstructure consists of very large colonies of columnar dendrites. No equiaxed grains were observed. In this range, $\Delta T_1^* < \Delta T < \Delta T_2^*$ and $t_{bu} > t_{pl}$ therefore no breakup occurred. At $\Delta T = 180$ K, $\Delta T > \Delta T_2^*$ and $t_{bu} < t_{pl}$ the microstructure was again composed of refined equiaxed grains superimposed on a substructure of spherical elements. Increasing the melt undercooling to $\Delta T = 282$ K had no significant effect on the microstructure, as the inequality $t_{bu} < t_{pl}$ was still valid. It is interesting to note that the solidification front speed increased from $\sim 20$ ms$^{-1}$ at $\Delta T = 180$ K to $\sim 30$ ms$^{-1}$ at $\Delta T = 282$ K (cf. figure 3).
Figure 3. Optical micrographs showing the microstructure of droplets of commercial Fe-Ni soft magnetic alloy P36 processed by EML and quenched on a copper substrate at melt undercoolings in the range $\Delta T = 0$ to 282 K.

4. Non-equilibrium solidification in Fe$_{90}$Ni$_{10}$ undercooled melts in microgravity
Some initial results showing the principal effects of microgravity on metastable phase formation of the Fe$_{90}$Ni$_{10}$ binary alloy in EML experiments are visualized in figure 4. In this example, the critical undercooling for the $\delta$-Fe metastable phase ($\Delta T_c \approx 70$ K) appears to be comparable for both terrestrial and microgravity conditions, which is inferred from the transition from single to double recalescence.

There is some indication that the lifetime of the metastable phase increases under microgravity conditions in parabolic flights (longer plateau of the recalescence curve), as has been previously reported for other alloy systems [11, 13]. This was attributed to the reduced fluid flow in the droplet under microgravity [7]. Despite the increased lifetime the metastable phase cannot be retained to room temperature in the Fe-Ni system and there is no independent proof of its presence, as in the Fe-Ni-Cr ternary alloy [14].

The addition of a high speed video camera to the TEMPUS EML facility has allowed visualisation of the solidification front under microgravity conditions. A series of images from the high speed camera shows the growth of the solid (bright) into the undercooled melt (darker) for $\Delta T = 29$ K during a parabolic flight (figure 5). In the images, the liquid droplet is partially obscured by the sample cup.
Solidification is complete 2.5 ms after triggering and an approximate front velocity of 0.6 m/s may be inferred from this. The striking feature of these images is that the solidification front is not smooth but contains highly angular sections, the shape of which is likely to be related to the crystal symmetry.

Full exploitation of the spatially resolved data from the camera requires more exact modelling of the solidification front geometry within the droplet. The angular solidification front may also be one contributing factor to the sizeable scatter between the recalescence curves of different experimental trials recorded by the photodiode, especially in the derived plateau times.

A further important application of the high speed camera was to measure the surface tension of the levitating droplet. During several parabolas, the surface oscillations of the droplets during the undercooling phase were recorded. The surface tension was extracted from these oscillations by the method described above. An average value of $\sigma = 1.90 \pm 0.01$ N/m at a mean temperature 1583°C was obtained. The surface tension of pure Ni is $\sigma = 1.73$ N/m and that of pure Fe is $\sigma = 1.90$ N/m at 1583°C. The value obtained for the Fe$_{90}$Ni$_{10}$ alloy fits well to a linear interpolation between the values for the pure elements and is in good agreement with literature data [14].

5. Summary and conclusions

The microstructure of an Fe-Ni based commercial soft magnetic alloy has been studied over a much larger range of undercooling than has been previously shown [3]. Transitions in the microstructure could be interpreted using the dendrite breakup model of Karma [6]. No further microstructural transitions were found at $\Delta T > \Delta T^*_2$. The role of convective fluid flow in producing these microstructural transitions may be studied by conducting experiments under microgravity conditions where the convection is reduced by an order of magnitude. Initial results from parabolic flight experiments showed the formation of a metastable phase during solidification of Fe$_{90}$Ni$_{10}$ at $\Delta T > \Delta T_c$. Some indication of differences in the lifetime of the metastable phase between terrestrial and microgravity experiments could be inferred. This may be related to the reduced fluid flow under microgravity. High speed video recordings during the parabolic flights showed that the solidification front is not planar but often highly angular. Accurate determination of the solidification front speed requires modelling of the front morphology. The surface tension of Fe$_{90}$Ni$_{10}$ alloy droplets was determined during the parabolic flights. The value of $\sigma = 1.90 \pm 0.01$ N/m obtained showed good agreement with literature values.

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Figure 5. Picture series from the high speed camera of parabolic flight experiments for Fe$_{90}$Ni$_{10}$. From the moving front of the solid (bright) into the 29 K undercooled melt (dark) the solidification velocity was evaluated.

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