



	Experiment title: Metastable phase formation in undercooled Nd-Fe based alloy melts	Experiment number: ME-668
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Shifts: 18	Local contact(s): Gabriela Gonzalez Aviles, Thomas Buslaps	<i>Received at ESRF:</i>
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Report:

Metastable crystallization products during solidification of undercooled Nd-Fe-B melts have investigated by energy-dispersive diffraction experiments on samples that were containerlessly processed by electromagnetic levitation. During our previous experiment HS-1740 on B-rich Nd-Fe-B alloys (at compositions used for high-performance permanent magnets based on the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ (Φ) phase) it was found that in the undercooled melt a metastable ternary phase is preferentially formed and that it triggers the crystallization of the stable $\text{Nd}_2\text{Fe}_{17}$ phase. The metastable phase can either be formed as a peritectic phase from pro-peritectic γ -Fe or as the primary solidifying phase in the deeply undercooled melt. Due to the rhombohedral symmetry of the metastable phase it was concluded that the structure is similar the stable binary $\text{Nd}_2\text{Fe}_{17}$ phase. In order to elucidate the relation between the stable $\text{Nd}_2\text{Fe}_{17}$ phase and metastable ternary phase in Nd-Fe-B alloys, in the present experiments binary Nd-Fe alloys and the effect of the addition of boron on phase formation have been investigated on 8 different alloy compositions. Diffraction spectra with an integration time between 5 to 10 seconds were taken in sequence during cooling and solidification as well as during the subsequent heating and remelting of crystalline phases. The temperature of the sample is measured by a pyrometer during the entire experiment cycle.

Binary $\text{Nd}_{12.5}\text{Fe}_{87.5}$ alloys solidify primarily in fcc-Fe (γ) as the pro-peritectic phase which is followed by the crystallization of the $\text{Nd}_2\text{Fe}_{17}$ phase as the peritectic phase. The Bragg peaks of the crystallizing $\text{Nd}_2\text{Fe}_{17}$ phase in binary Nd-Fe and that of the metastable ternary phase in Nd-Fe-B alloys of all compositions investigated can be indexed on the same rhombohedral crystal structure as revealed by stable the $\text{Nd}_2\text{Fe}_{17}$ phase at room temperature (prototype $\text{Zn}_2\text{Th}_{17}$). The lattice constants of both $\text{Nd}_2\text{Fe}_{17}$ and the metastable ternary phase obtained from diffraction spectra at the same temperature are quite similar. These results suggest a composition of $\text{Nd}_2\text{Fe}_{17}(\text{B})$ (in the following denoted as χ) for the metastable phase, i.e. it reveals the same $\text{Zn}_2\text{Th}_{17}$ -type crystal with B atoms at interstitial lattice sites similar to the C atoms as known for the stable $\text{Nd}_2\text{Fe}_{17}(\text{C})$ compound.

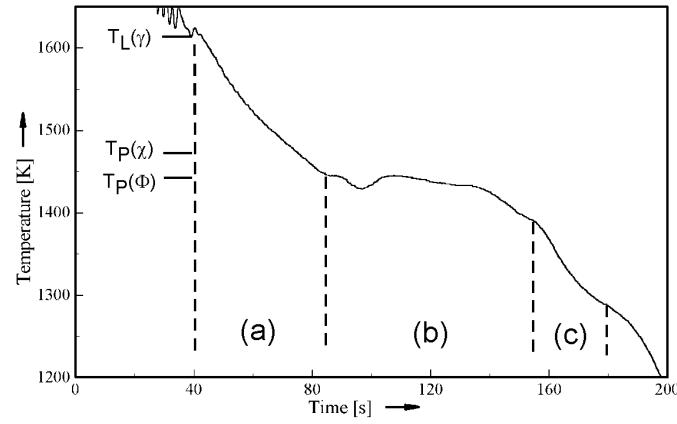
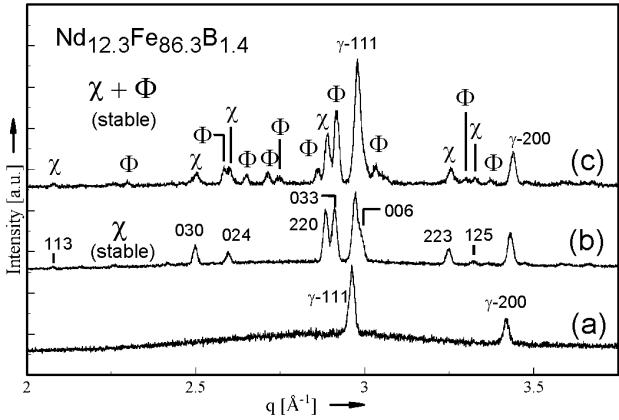


Fig. 1: Sequence of the crystallizing phases γ -Fe, stable χ ($\text{Nd}_2\text{Fe}_{17}\text{B}$) and stable Φ ($\text{Nd}_2\text{Fe}_{14}\text{B}_1$) and the corresponding temperature-time profile. Single spectra were taken at an integration time of 5 s and were added within the time period (a), (b) and (c).

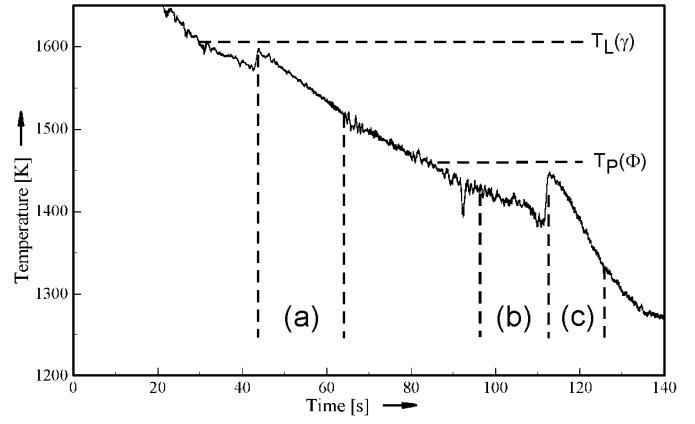
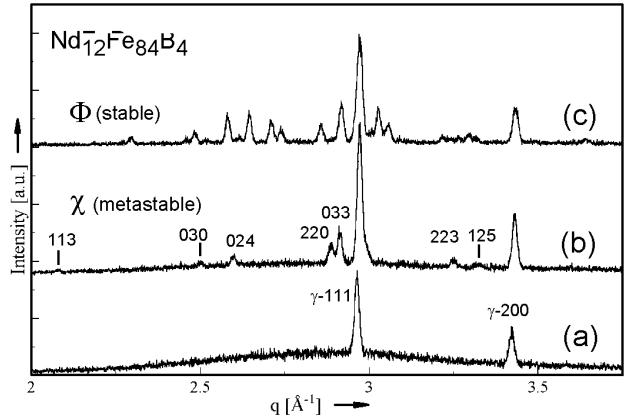


Fig. 2: Sequence of the crystallizing phases γ -Fe, metastable χ ($\text{Nd}_2\text{Fe}_{17}\text{B}$) and stable Φ ($\text{Nd}_2\text{Fe}_{14}\text{B}_1$). The metastable χ -phase exists for approx. 15 s (period (b)) and initiates the crystallization of Φ -phase in the residual undercooled liquid.

By the addition of small amounts of B to Nd-Fe alloys the ternary $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ compound occurs as a second peritectic phase. The in-situ diffraction experiments during cooling of a $\text{Nd}_{12.3}\text{Fe}_{86.3}\text{B}_{1.4}$ alloy in Fig. 1 show the sequence of crystallizing phases, i.e. γ -Fe, $\text{Nd}_2\text{Fe}_{17}$ (or $\text{Nd}_2\text{Fe}_{17}\text{B} = \chi$) and the $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ phase. Both peritectic phases remain in the solidified sample and disappear only when heating in the reversal sequence at the peritectic temperature $T_P(\Phi)$, $T_P(\chi)$ and the liquidus temperature $T_L(\gamma)$, respectively. From this observation it is concluded that both the $\text{Nd}_2\text{Fe}_{17}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ are thermodynamically stable.

With increasing B concentration of the alloy the $\text{Nd}_2\text{Fe}_{17}\text{B}$ phase becomes metastable as it is shown by the results on alloys with 4 at. % B (Fig. 2). Under equilibrium conditions these alloys exhibit a single peritecticum with the stable $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ as the peritectic phase. As it was found in the previous experiments on B-rich alloys (HS-1740) the formation of the peritectic $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ phase is frequently suppressed and does not always set in at the peritectic temperature $T_P(\Phi)$. Instead, the metastable phase is formed below $T_P(\Phi)$ followed by the crystallization of the stable peritectic phase in the residual liquid that is still undercooled. The deviation from the thermodynamic equilibrium is revealed the steep temperature rise (recalrescence) of the sample to the solidification temperature of $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ when the heat of fusion is released (Fig. 2, between period (b) and (c)). Now the spectrum reveals the Bragg peaks exclusively of the phases Φ and γ while those of the $\text{Nd}_2\text{Fe}_{17}\text{B}$ phase are vanishing. The Φ -phase disappears only when reheating to $T_P(\Phi)$. Apparently, the $\text{Nd}_2\text{Fe}_{17}\text{B}$ phase is metastable with a lifetime limited to some seconds.

From the diffraction experiments it can be concluded that the metastable phase in Nd-Fe-B alloys is a ternary extension of the stable $\text{Nd}_2\text{Fe}_{17}$ phase with a similar crystal structure, i.e. the ordered $\text{Zn}_2\text{Th}_{17}$ -type structure. The ordered structure can be identified by the presence of the superstructure (024)-reflection whereas it disappears for its disordered modification that is known to be of the hexagonal Tb_1Cu_7 -type.