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Report:

Phase formation in undercooled Nd-Fe-B alloy melts have been investigated by in-situ diffraction using synchrotron radiation on electromagnetically levitated samples during solidification. Nd-Fe-B alloys are used for the development of high-performance permanent magnets which are based on the intermetallic compound $Nd_2Fe_{14}B_1$ (ϕ-phase) exhibiting extraordinary hard magnetic properties. Under equilibrium solidification conditions alloys near the stochiometric composition of $Nd_2Fe_{14}B_1$ solidify in the γ-Fe solid solution followed by the peritectic formation of the ϕ-phase. From microstructural analysis of samples it is known that solidification of Nd-Fe-B melts frequently involves metastable phases. However, the metastable crystallization products in Nd-Fe-B alloys could not be retained due to the decomposition into stable phases during cooling from solidification to the ambient temperature.

During the experimental campaign HS-1740 the electromagnetic levitation technique for containerless processing and undercooling of metallic melts was combined with energy-dispersive diffraction experiments. The peritectic alloys compositions $Nd_{11.8}Fe_{82.3}B_{5.9}$ and $Nd_{14}Fe_{79}B_7$ as well as $Nd_{18}Fe_{73}B_9$ alloys which are of equilibrium ϕ-phase solidification type have been investigated. On the freely suspended liquid samples it was possible to observe directly alternative solidification pathways and the appearance and the decay of metastable phases. In particular, it was found that there exists a metastable phase with a rhombohedral structure. It can be formed either as an intermediate phase between the crystallization of the stable phases γ and ϕ or as the primary solidifying phase in deeply undercooled melts. The lattice constants of approximately $a = 0.865$ nm and $c = 1.341$ nm are similar to that of the rhombohedral Nd_2Fe_{17} phase that is stable in binary Nd-Fe alloys.

As an example Fig. 1 shows a temperature-time-profile during solidification of a peritectic $Nd_{14}Fe_{79}B_7$ sample with an intermediate metastable solidification product. The temperature rises (recalescence) reveal different crystallization steps due to the released heat of fusion. Diffraction spectra with an integration time of 10 seconds were taken in sequence so that the formation of crystalline phases is observed in-situ and correlated to the recalescence events. Near the liquidus temperature T_L solidification sets in with the crystallization of stable γ-Fe. As shown in Fig. 1, it is frequently observed that the formation of the stable peritectic ϕ-phase does not occur at the peritectic temperature T_P as it is expected in thermodynamic equilibrium. Instead, a metastable phase (MS) is formed at a temperature about 50 K below T_P and then followed by the stable ϕ-phase. Now the spectrum exhibits clear reflections of ϕ, whereas the metastable phase is no longer present which is presumably due to remelting or decomposition.

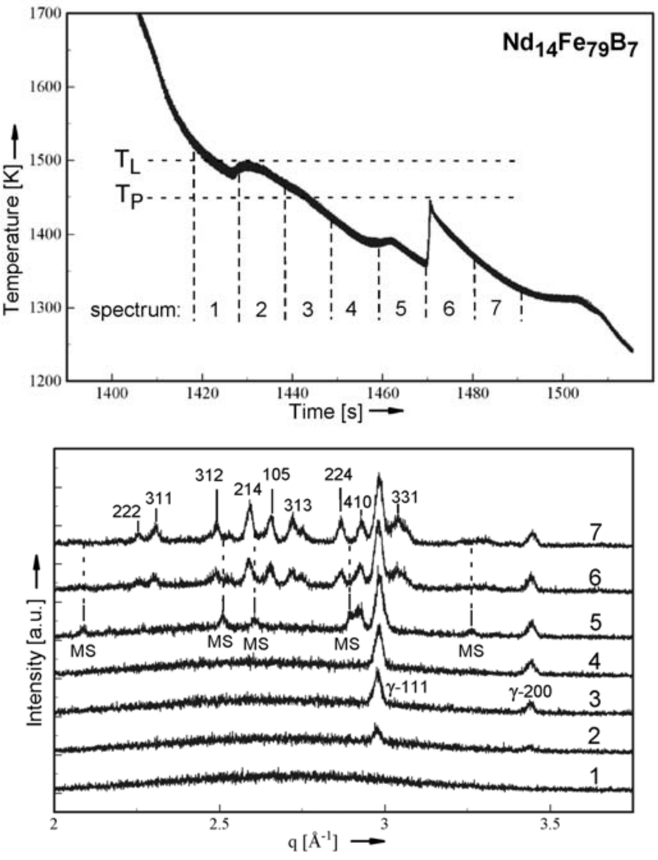

Fig.1: Temperature-time profile and corresponding diffraction pattern during solidifcation of a $Nd_{14}Fe_{79}B_7$ sample showing an intermediate metastable phase (MS) between the stable phases γ and ϕ. The reflections of ϕ are indexed in spectrum no. 7.

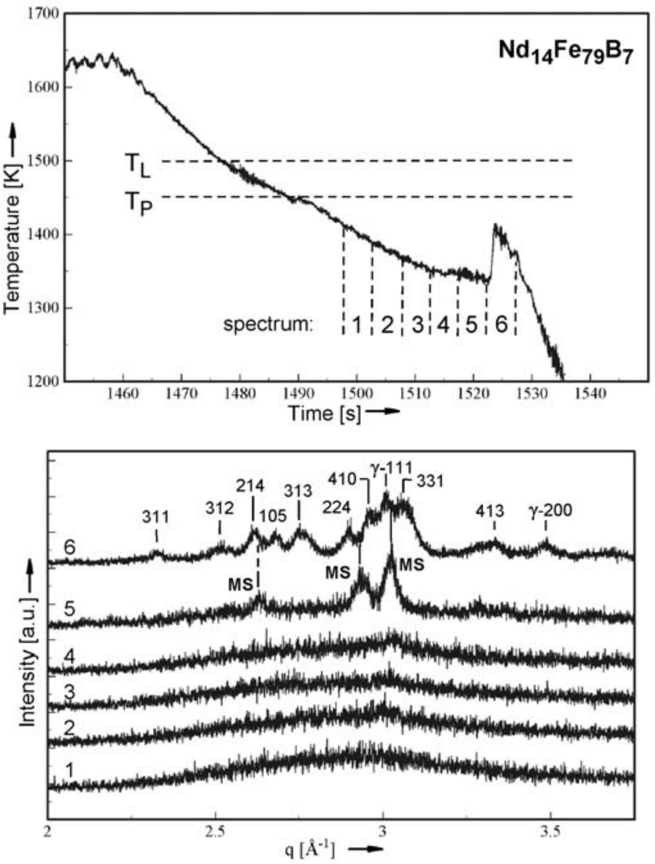

Fig.2: Temperature-time profile and diffraction pattern showing the primary crystallization of the metastable phase (MS) in the undercooled melt at about 150 K below the liquidus temperature T_L.

If the melt is undercooled prior to solidification the crystallization of the stable γ-phase is suppressed with rising degree of undercooling. As shown in Fig. 2 solidification consists of two steps and is initiated by a weak plateau in the temperature-time profile between spectrum 4 and 5 which is not due to the stable γ-phase but caused by the primary solidification of the same metastable phase. The $Nd_2Fe_{14}B_1$ -phase is formed during the second recalescence. Besides the reflections of ϕ-phase the corresponding diffraction spectrum now reveals the reflections of γ-Fe whereas the primary metastable phase can not be detected. This observation indicates that the metastable phase is decomposed into the stable phases γ-Fe and $Nd_2Fe_{14}B_1$. This assumption leads to the conclusion that it is a ternary phase. A single spectrum usually does not contain all Bragg peaks due to textures and the limited volume fraction of the solid phase. Comprising all spectra, the metastable phase exhibits all prominent reflections of the rhombohedral Nd_2Fe_{17} -phase.

Obviously, the metastable rhombohedral phase plays a decisive role during solidification of Nd-Fe-B melts and is formed in a direct competition to the hard magnetic $Nd_2Fe_{14}B_1$ phase which crystallizes in a subsequent step. The experimental results on peritectic alloys obtained so far do not reveal that the ϕ-phase crystallizes directly from the undercooled melt without the primary solidification of γ or the rhombohedral phase. Similar to the peritectic alloys, the primary solidification of the rhombohedral phase was also found in non-peritectic $Nd_{18}Fe_{73}B_9$ alloys if a critical undercooling level is exceeded. So far, the metastable ternary phase is not known exactly but from the diffraction studies it is concluded that it is related to the rhombohedral Nd_2Fe_{17}-phase.