ESRF	**Experiment title:** Short-Range Order And Phase Selection in Undercooled Liquids	**Experiment number**: HS-1593
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Shifts: 15	**Local contact(s)**: Thomas Buslaps, Sandrine Schlutig, Veijo Honkimaki	*Received at ESRF:*

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Report:

It is meanwhile well established that metallic melts can be deeply undercooled below their equilibrium melting temperature. Such undercooled liquids are in a metastable state, from which under special conditions metastable solid structures may be formed during solidification.

The alloy system Ti-Fe-Si-O forms a great variety of stable and metastable solid phases including structurally complex phases such as quasicrystals and their approximants. The competition of this large number of different phases implies a complicated phase selection behaviour during solidification, which depends on alloy composition and undercooling.

During or experiment HS-1593 we successfully performed *in situ* investigations on the phase selection during solidification of Ti-Fe-Si-O melts as a function of the temperature and the alloy composition. The liquids were containerlessly processed and undercooled by utilization of the electromagnetic levitation technique which was combined with an energy dispersive X-ray diffraction (EDXD) setup at beamline ID15a in order to directly determine the crystal structure of the solid phases formed during solidification with a time resolution of 1-2 seconds. Moreover, EDXD was also utilized to study the short-range order of various Ti-Fe-Si-O melts as a function of the temperature.

As an example, Fig. 1 shows the results of investigations of the phase selection behaviour of a $Ti_{66}Fe_{28}Si_2(SiO_2)_4$ melt. The inset of the figure depicts the temperature-time profile of this experiment. Two different solidification events are indicated by rises of the temperature (recalescence) due to the release of heat of fusion when a solid phase crystallizes. Spectrum 1 was recorded before the first recalescence event and shows the typical diffractogram of a liquid. During the first recalescence α-Ti crystallizes primarily from the undercooled melt as indicated by its characteristic Bragg peaks in spectrum 2, which was acquired after the first recalescence. In the second recalescence event the rest of the liquid and α-Ti transform under formation of Ti_2Fe, which is proven by spectrum 3 that was recorded directly after the second solidification step. If the specimen is cooled to a lower temperature, a solid-state phase transformation is observed (spectrum 4) in which

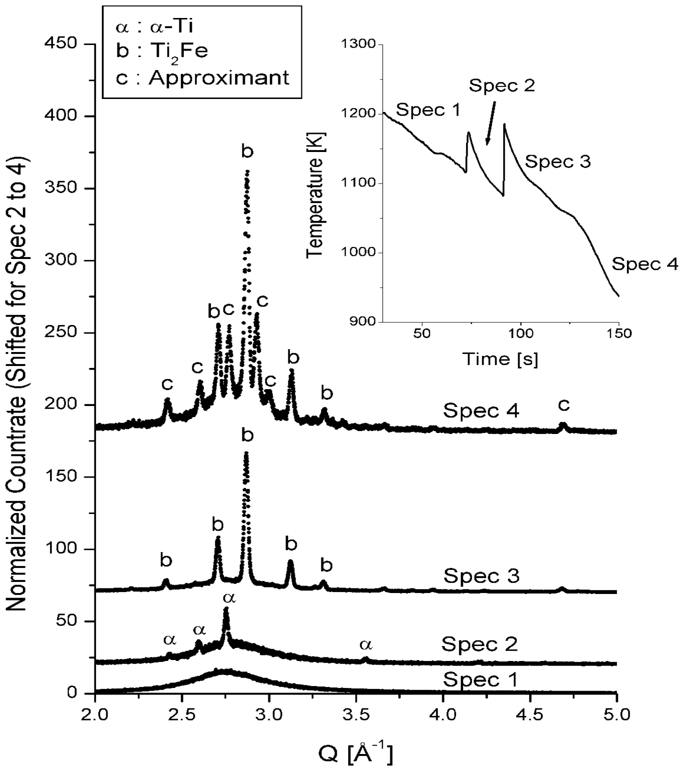

Fig. 1 EDXD spectra recorded at different times during an undercooling experiment at a $Ti_{66}Fe_{28}Si_2(SiO_2)_4$ sample. The temperature-time profile of the experiment is shown in the inset.

the (1/1) approximant phase that is structurally closely related to the metastable icosahedral quasicrystalline phase in Ti-Fe-Si-O, is formed. Due to the fact that the primarily formed phase (α-Ti) transformed completely during the subsequent phase transformations it cannot be identified in the as solidified material. However, the fast *in situ* diffraction experiments possible at ESRF enabled to determine the phase selection sequence during solidification in an unambiguous way.

For some alloy compositions we were able to observe changes of the phase selection sequence of Ti-Fe-Si-O alloys depending on the undercooling of the liquid. Fig. 2 shows such results obtained during two different cooling cycles at a $Ti_{66}Fe_{28}(SiO_2)_6$ sample. The insets of the figures again show the temperature-time profiles of the cycle. In the case of the experiment shown in Fig. 2a the melt was undercooled up to a temperature of T=1260 K. Then a first solidification event (step 1) sets in. Approximately 15s later a second recalescence (step 2) is observed, which indicates a second phase transformation. The X-ray diffractograms taken before the first recalescence, between the first and the second recalescence and after the second recalescence (Fig. 2a) exhibit that during the first recalescence α-Ti is primarily formed from the undercooled liquid. During the second recalescence event two phases, FeTi and Ti_2Fe, are simultaneously formed from the rest of the liquid. As seen in Fig. 2b the phase-selection behaviour changes significantly, if a deeper undercooling is achieved. In this case the melt was undercooled up to 1190 K and solidifies during one single recalescence event. By EDXD it was proven, that the (1/1)-approximant phase is formed during solidification from the deeply undercooled liquid.

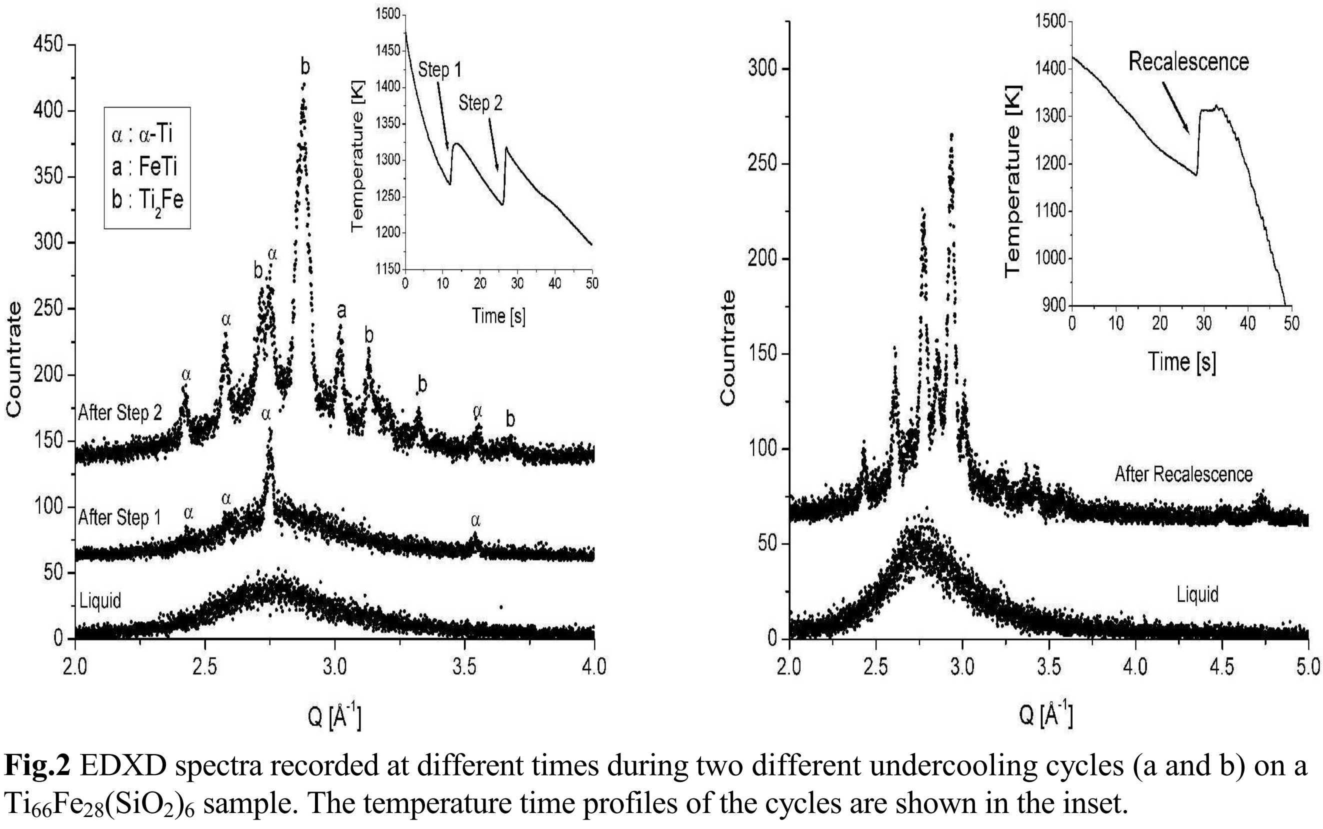

Fig.2 EDXD spectra recorded at different times during two different undercooling cycles (a and b) on a $Ti_{66}Fe_{28}(SiO_2)_6$ sample. The temperature time profiles of the cycles are shown in the inset.