	Experiment title: In-situ X-ray diffraction experiments on the phase selection during solidification of Al-Ni and Ti-Al-Ta melts	**Experiment number**: **HS-3559**
Beamline: ID15A	**Date of experiment**: from: 12.03.2008 to: 18.03.2008	**Date of report**:
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Report:

The experiments performed within this beamtime contributed to the European Integrated Project IMPRESS, an acronym for 'Intermetallic Materials Processing in Relation to Earth and Space Solidification', aiming to develop advanced Al-Ni based catalytic powders for use in hydrogen fuel cell electrodes and hydrogenation reactions and to optimise the casting processes and post-solidification heat-treatment of Al-Ti based alloys, in order to deliver high-quality turbine blades.

Energy dispersive X-ray diffraction experiments on different Al-Ni and Ti-Al-Ta melts have been performed at beamline ID15A of ESRF, with the goal to investigate the phase selection during non-equilibrium solidification of undercooled Al-Ni melts as a function of undercooling and alloy composition [1,2] and to determine the high temperature phase equilibria at temperatures above T > 1400°C for selected Ti-Al-Ta alloys [3]. In oder to undercool the melts significantly below the melting temperature and to avoid chemical reactions of the melts with crucible materials, the melts were containerlessly processed within an electromagnetic levitation facility specially designed for this type of experiments. The experimental setup is described elsewhere [4].

As an example for studies of the non-equilibrium solidification of Al-Ni melts, here results obtained for the the Raney-type alloy $Al_{68.5}Ni_{31.5}$ are shown. For this alloy, under equilibrium solidification conditions the AlNi phase primarily forms from the melt, which subsequently transforms into Al_3Ni_2 at the peritectic temperature T_{p1} = 1406 K. At T_{p2} = 1127 K a second peritectic reaction occurs, during which Al_3Ni is

formed. Fig. 1 shows results of an in-situ diffraction experiment on a $Al_{68.5}Ni_{31.5}$ sample during non-equilibrium solidification. In the inset the temperature-time profile is shown. The different colours in the temperature-time profile mark the time intervals during which the corresponding diffractograms plotted in the same colour were recorded. Starting at a temperature above the liquidus temperature T_L = 1603 K, the melt has been cooled and undercooled up to T_N = 1290 K as also confirmed by the diffuse X-ray diffraction intensity maxima typical of a liquid phase. At T_N crysatllization sets in as indicated by a sudden temperature rise (recalescence) in the temperature-time profile due to the release of heat of fusion. During this phase transformation ß-AlNi is formed as indicated by two distinct peaks emerging in the X-ray diffractogram. Subsequently AlNi transforms by peritectic reaction under formation of Al_3Ni_2. The sequence of phase formation up to this point is the same as found under solidification conditions close to equilibrium or at intermediate levels of undercooling [2], although a deep undercooling of $\Delta T = T_L - T_N$ = 313 K is reached. However, when passing T_{p2} during further cooling the formation of the Al_3Ni phase observed under close to equilibrium solidification conditions does not occur. Instead, a metastable phase crystallizes at a temperature T_{N3} below T_{p2}, corresponding to an undercooling of the peritectic reaction of $\Delta T_2 = T_{p2} - T_{N3}$ = 155 K. The diffraction peaks from this phase are characteristic of the decagonal quasicrystalline D-phase as found in a splat quenched Al-Ni alloys [5]. For a few seconds three clear reflections of this phase coexist with the Al_3Ni_2 phase at almost constant temperature. Their intensity drops when the reflections of equilibrium phase Al_3Ni appear. This entails the second recalescence event during which the D-phase is rapidly and completely decomposed or remelted, while Al_3Ni_2 is formed. Our investigations [1] have shown that the metastable D-phase is only formed if a sufficient undercooling of the second peritectic reaction by $\Delta T_2 \approx 150$ K below the peritectic temperature T_{p2}, is reached. Otherwise the Al_3Ni equilibrium phase nucleates and the D-phase does not appear.

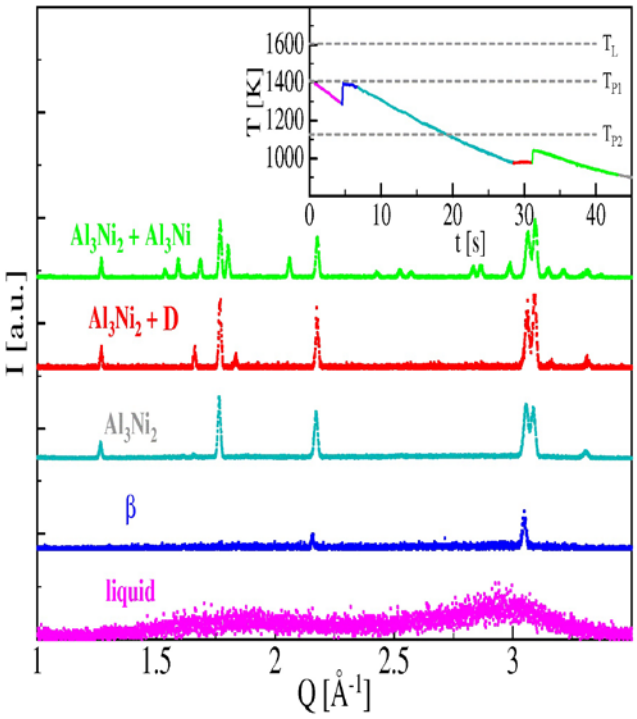

Fig. 1: X-ray diffractograms measured during non-equilibrium solidification of an $Al_{68.5}Ni_{31.5}$ alloy melt. The inset shows the temperature-time profile of the experiment cycle. The different colours mark the time intervals during which the diffractograms plotted in the same colour were recorded.

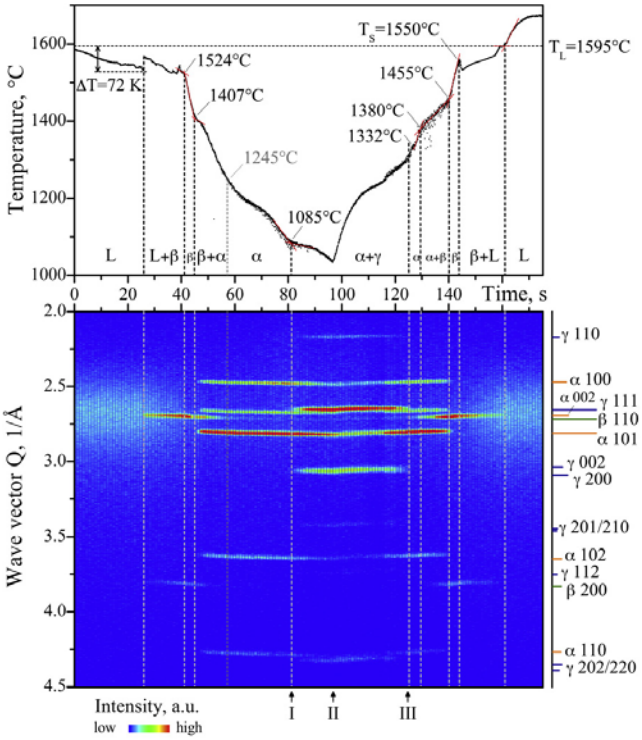

Fig. 2: Time evolution of the temperature (top) and in situ X-ray diffraction patterns (bottom) for a cooling/heating cycle on a $Ti_{48.9}Al_{43.9}Ta_{7.2}$ alloy [3].

Apart from studies on the non-equilibrium solidification of Al-Ni alloy melts, we have investigated the phase equilibria of the Ti-Al-Ta alloy system at high temperature by in situ X-ray diffraction [3]. For the Ti-Al-Ta system information on liquid/solid phase equilibria, such as liquidus and solidus surfaces, or invariant reactions, has been scarce due to the high chemical reactivity of the melts. A couple of systematic studies on the solidification behaviour in 15 Ti-Al-Ta alloys [6,7] estimated a liquidus surface in the region around γ-TiAl. The primary solidifying phases (e.g., bcc ß or hcp α) are not preserved due to solid state transformations, and were determined solely by examining the symmetry (4- or 6-fold, respectively) of the primary dendrites in the as-cast microstructure of arc-melted ingots. Our in-situ X-ray diffraction experiments provide the first direct observations of phase transformations in Ti-Al-Ta alloys at elevated temperatures up to complete melting. As an example, fig. 2 shows temperature-time profile (top) and the corresconding X-ray diffraction patterns (bottom) for the a cooling/heating cycle on a $Ti_{48.9}Al_{43.9}Ta_{7.2}$ alloy. Prior to the observed cycle the sample was heated well above the liquidus temperature, T_L, to ensure complete melting, evidenced by the diffuse first intensity maximum of the EDXD pattern around Q = 2.65 $Å^{-1}$ Different phase transformations are identified as indicated in the figure. Noteworthy are the observed differences of the phase transition temperatures during cooling and heating, which are due to undercooling of the phase transformations during cooling. The phase transformations and phase transition temperatures determined from the in situ experiments for different Ti-Al-Ta alloys at high temperature during heating are given in table 1. This experimental data have been used for developing a thermodynamic description of the ternary Ti-Al-Ta system [8].

Table 1: Phase transformations and phase transformation temperatures determined by in situ X-ray diffraction on levitated Ti-Al-Ta samples during heating [3]

Alloy	Phase transformation	Transformation Temperature [°C]
$Ti_{48.9}$ $Al_{43.9}$ $Ta_{7.2}$	liq. → liq. +ß	1635
	liq. + ß → ß	1570
	ß → α + ß	1458
$Ti_{47.8}Al_{45.2}Ta_{7.0}$	liq. → liq. +ß	1617
$Ti_{27.3}Al_{55.6}Ta_{17.1}$	liq. → liq. +ß	1470
$Ti_{20.5}Al_{48.9}Ta_{30.6}$	liq. → liq. +ß	1680
$Ti_{26.9}Al_{58.4}Ta_{14.7}$	liq. → liq. +α	1560

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