ESRF	**Experiment title:** **Establishing the transformation pathways in Refractory Metal High Entropy Superalloys**	**Experiment number**: MA4990
Beamline: ID15A	**Date of experiment**: from: 7/12/21 to: 9/12/21	**Date of report**: February 2022
Shifts: 6	**Local contact(s)**: G Vaughan	*Received at ESRF:*

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Report:

Refractory metal high entropy superalloys (RSA) are a new class of materials that show exceptional promise for high temperature applications. However, the pathway that leads to the formation of their two-phase A2-B2 microstructure remains unclear and subject to considerable debate. Within the literature, most of the proposed transformation sequences include a spinodal decomposition but the material must also undergo an ordering reaction to produce the A2-B2 microstructure reported at room temperature. Consequently, it is imperative to the field that the sequence in which these transformations occur and their related temperatures are directly and unambiguously determined. This experiment sought to provide such data through the use of *in situ* Laue diffraction. Five alloy samples with systematically varying compositions were prepared and 5 mm diameter, 1 mm thick discs with large grain sizes were extracted from these mateirals so as to enable the complete immersion of a polychromatic beam within a single crystal.

The externally provided equipment was successfully installed into the beamline (Fig. 1) and ceria calibration data collected. Following this, a reference temperature cycle was performed using a pure Ni specimen. Samples were heated and cooled between 20 and 1200˚C using a Linkam 1500V stage at $10^{\circ}C.min^{-1}$ whilst collecting Laue diffraction patterns approximately every 30 s. To avoide oxdiation all experiments were performed under flowing Ar.

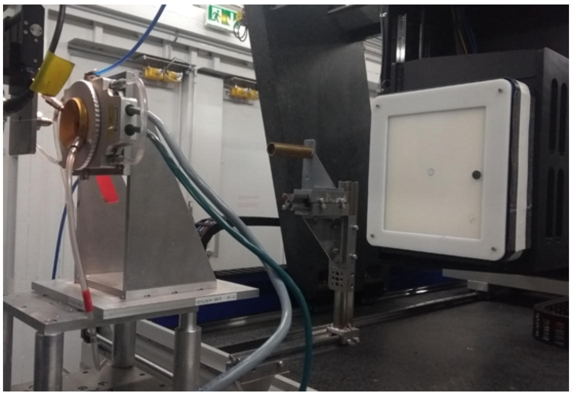

Fig. 1 – Linkam stage installed on ID15A

Unfortunately, when collecting data from the RSA samples during the first overnight run, the Laue signal showed signficant streaking along particular directions. As would be expected, the extent of this streaking increased as the samples were heated, effectively obscuring the patterns and preventing unambiguous observation of the phase transformations as intended.

The source of the streaking was attributed to two key factors; 1) the large nunmber of small precipitates that intersected the beam path; and 2) the substantial inter-phase strain that exsists between the A2 and B2 phases, which is on the order of 5%). In an attempt reduce the impact of sample thickess (issues 1), samples from two key alloys were mechanical ground to reduce the material in the beam path. Data collected from these thinned samples were a little sharper but significant streaking still remained, suggesting that the effect was dominated by the inter-phase misfit strain. That this strain would essentially obscure the diffraction pattern had not been anticipated by either the experimental team or the instrument scientists.

When discussing the issue with the local contact, they informed us that the high energy monochromatic diffraction patterns from the test samples sent ahead of the experiment had yielded good signal. As such, in an attempt to collect useful data, the beamline configuration was changed from polychromatic operation to monochromatic mode. Following the change, it was apparent that the large Ewald sphere provided by the high incident beam energy would enable the acquisition of diffraction patterns that were ideal data for studying the desired phase transformations, provided that suitably oriented crystals could be identified within the samples. Unfortunately, since the samples for this experiment had been produced for a polychromatic Laue experiment they had not be cut along specific orientations nor had spatial-orientation data been acquired. Nevertheless, through persistance and careful stage rotation, it was possible to collect data close to the [100] zone axis for one of the model alloys (Ti-25Ta-25Zr-10Al), see Fig. 2.

The initial room temperature microstructure of this material (left image in Fig. 2) contained more reflections than had been expected, which has prompted further complimentary *ex situ* studies through transmission electron microscopy. To take advantage of this well oriented grain, diffraction patterns were collected over a number of heating and cooling cycles. The data showed clear evidence of phase transformation, for example through the absence of many reflections seen at room temperature when at ~900˚C (right image in Fig. 2). Detailed fitting of individual reflections is currently underway, attempting to track intensity as a function of temperature to provide direct evidence of the transformation sequence and relative temperature. However, this effort is complicated by the fact that the patterns were not acquired directly along a zone axis, which combined with compounding thermal effects during heating, influence the observed intensity.

It is anticipated that it will be possible to extract enough novel information about the nature of the transformation pathway of Ti-25Ta-25Zr-10Al from these data to produce a journal publication. However, the streaking issues encountered with the Laue data and the lack of oriented samples for the monochromatic beam investigation mean that many of the key objectives stated in the original proposal were not met. As such, the investigators intend to follow up in a subsequent round and request access to perform further rmonochromatic experiments on specifically oriented samples.

The experimental team would like to take this opportunity to thank the local contact (G. Vaughan) for his assistance, advice and excellent technical expertise throughout the experiment.

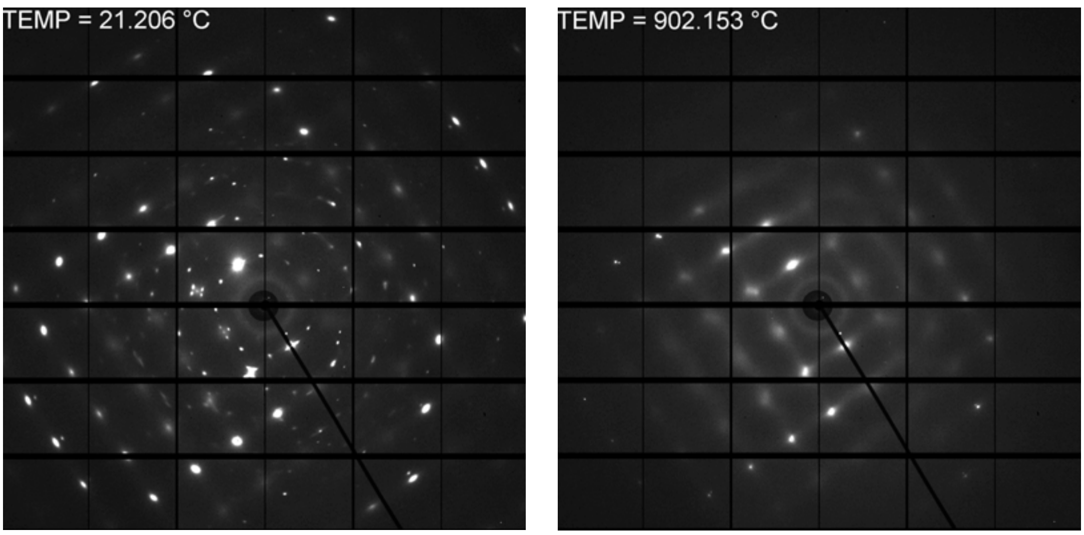

Fig 2. Experimental data from close to the [100] zone of Ti-25Ta-25Zr-10Al at 21˚C and 902˚C.