ESRF	**Experiment title:** **Oxidation of vicinal binary alloy surfaces**	**Experiment number**: SI-1575
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Report:

Aims of the experiment and scientific background

Ultra-thin aluminium-oxide layers are used as model catalysts, tunnelling barriers, corrosion barriers and thermal barrier coatings. Knowledge about the atomic structure of these layers is crucial for obtaining a better fundamental understanding of their functionality as well as their stability and performance if integrated in devices. Recently, much effort was put in the structure determination of the complex thin aluminium-oxide film on the binary alloy NiAl(110) [1,2], making it an ideal model system.

In this experiment we extended the research of NiAl oxidation and investigated the oxidation behaviour of a vicinal surface. This allows us to shed light on the role of defects as step sites and kinks in the oxidation process and to make one step further towards technologically more relevant systems like polycrystalline materials or alloy nanoparticles.

The aim of the experiment was to study the oxygen-induced segregation profile of vicinal NiAl(110) surfaces and the subsequent formation of oxide layers, both as a function of oxygen partial pressure and temperature. For this purpose we used a NiAl(671) surface, which is schematically depicted in Figure 1a. The investigation of such a surface raises the following specific questions: 1) What is the atomic structure of the clean surface in UHV. 2) What is the faceting behaviour of such a surface as a function of temperature and oxygen pressure. 3) How does the substrate influence the twin-formation in the thin film.

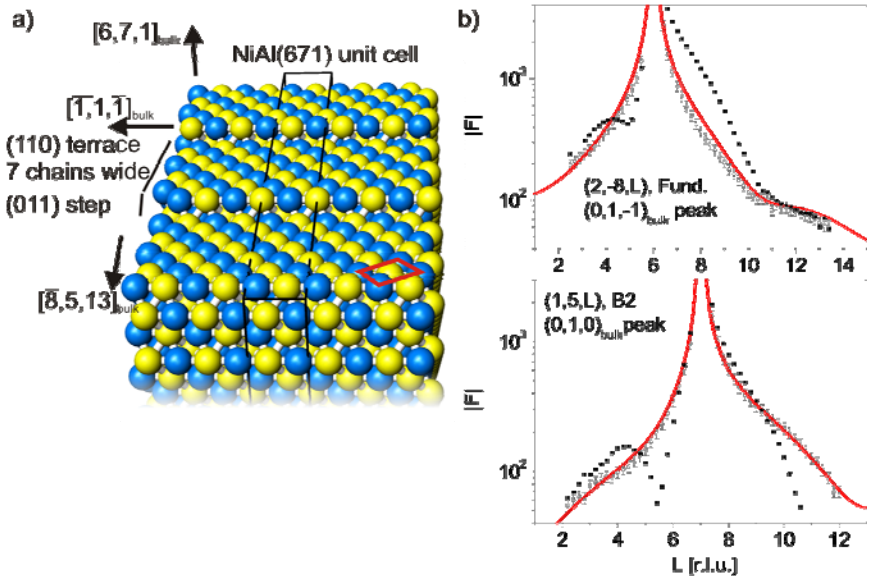

Figure 1 a) Model of the NiAl(671) unit cell. A (1,1,0) inplane unit cell is marked red on the terrace. b) A fundamental (top) and a B2-ordered type CTR of the clean (open circles) and the oxidized but not annealed (solid squares) surface, together with the fit (red line).

Experimental details and results

The in-situ surface x-ray diffraction (SXRD) measurements were carried out in horizontal geometry in the second hutch of ID03 where – after the removal of the flight tube in front of the detector- it is possible to mount our portable UHV chamber in which the in-situ measurements were performed. The data were measured with a point detector, using an x-ray energy of 15 keV.

In total, 224 structure factors, rendering 4 Crystal Truncation Rods (CTR), were recorded for the clean NiAl(671) surface as well as for the oxidized one (p_{O2} = 6E-6 mbar, T = 540 K, t_{ox} = 900s). Two of the CTRs are displayed in figure 1b together with a real space model of the (671) surface. The data of the clean surface are already analyzed while the fit (red line in figure 1) is based on a model similar to the (110) surface with additional lateral relaxation needed for the atoms at the step edge. Lateral relaxation was found to be a key ingredient for vicinal surfaces, as shown in a study of the Pt(977) surface [3]. For the oxidized surface the signal of the CTRs changes distinctively, which is related to oxygen-induced Nickel anti-sites forming in the interface region. The analysis of this phenomenon is still in progress as it is more complex compared to the case of the clean surface. Yet, the changes demonstrate that SXRD is a suitable tool for to study vicinal surfaces.

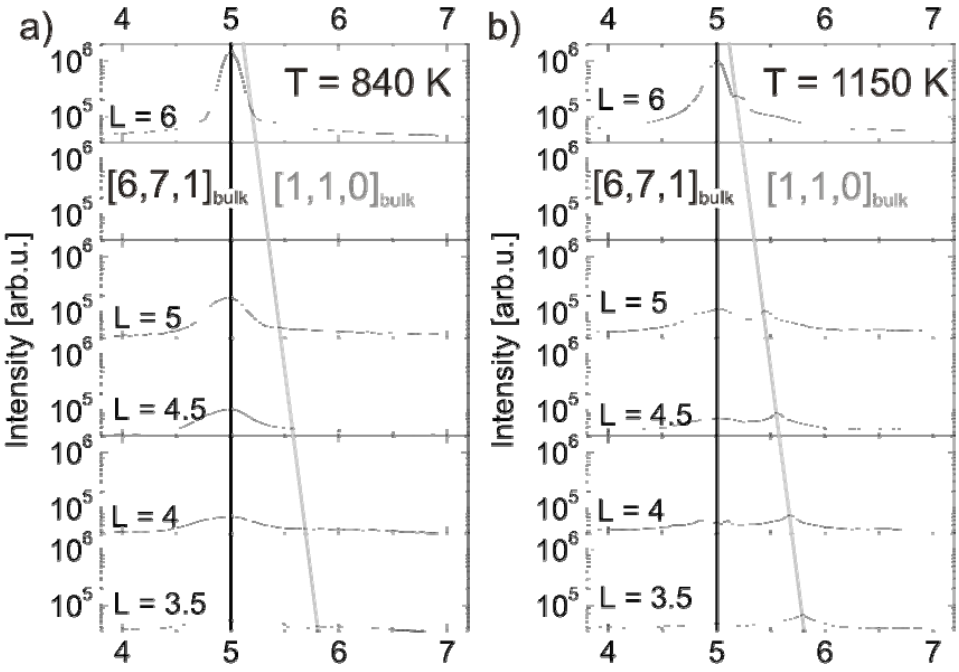

Figure 2 The oxidized sample was heated stepwise in UHV. K-scans across the steps were performed along the (15L) CTR before (a) and after (b) the faceting. At 1150 K a clear peak arises along the [1,1,0] direction (grey line) while the intensity along the surface normal decreases.

After the oxidation of the sample the temperature was increased step-wise. Thereby the formation of (110) facets at the surface, caused by the ordering of the oxide, was observed to take place at T = 1150 K as shown in extracts in figure 2. Furthermore, we found an asymmetry in the coverage of the two possible oxide domains on the stepped surface but a full interpretation is not finished yet.

Conclusion

The experiment showed that the recording of the extremely weak CTRs of a vicinal binary alloy surface is feasible at ID03, making a quantitative analysis possible. Reverting to the initial questions raised in the introduction: 1) A structural model of the clean (671) surface shows lateral relaxations at the step edges additional to the vertical ones. 2) The temperature dependent (110) faceting of the surface and hence the formation of an ordered oxide was observed to take place around 1150 K. This means that the first two of our goals as set for this experiment are satisfyingly met. The results for a structural model for the oxidized but not annealed surface as well as for the effect of the suppression of one oxide twin-domain (point 3 from the introduction) on stepped surfaces are presently being worked out. Future studies are needed to get more detailed information on the lateral relaxations near the kinks as well as the temperature dependence of oxygen-induced segregation of Ni-anti-sites. The results obtained so far pave the way for such investigations.

References

[1] A. Stierle *et al.* Science **303** (2004) 1652
[2] M. Kresse *et al.* Science **308** (2005) 1440
[3] P. Steadman *et al.* Phys. Rev. B **64** (2001) 125418