



	Experiment title: GIXD study of the structure and formation of thin Ni ₃ Al and NiAl films on Ni(111).	Experiment number: SI-1669
Beamline: ID3	Date of experiment: from: 02/07/2008 to: 11/07/2008	Date of report: 15/09/2008
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Report:

Among the different ordered compounds of Ni-Al, NiAl and Ni₃Al display remarkable mechanical and thermal properties. They also are resistant to corrosion, this latter property being due to the formation at their surface of a thin passive film of aluminium oxide that acts as a diffusion barrier. Ultra-thin aluminium oxide films that form on crystalline NiAl or Ni₃Al may also be obtained well-structured and used as model supports of small metallic aggregates. The aim of experiment SI1669 on ID3 was to determine, through GIXD measurements, the kinetics of Ni-Al alloy formation from Al deposits on Ni(111).

The experiment has been very successful. We have had the possibility of working on EH2 since June 23, without X-Rays. During this week of preparation, we have checked the different equipments on the UHV chamber: Al evaporator, Auger Spectrometer (AES), quartz microbalance and ion gun. The various problems encountered during this week have generated three opening of the chamber, followed by bake-out. This was very time consuming, but at the beginning of the allocated beamtime, the chamber was fully operating, and the evaporator was calibrated through Auger measurements.

We have worked on two samples, sample A, presenting a high density of steps, and sample B, with a small miscut. These two samples had been already studied at the INSP by other techniques (AES, LEED, SPALEED, STM and RBS-channeling). During the shifts allocated, we have performed nine Al deposits (D1 to D9) at room temperature. The first 6 deposits were performed on sample A, the last 3 deposits on sample B. Between two deposits, the sample is always sputtered and annealed except between D3 and D4. Table 1 summarizes the deposits.

We have particularly studied the Ni-Al thin alloy films on sample A. Results from the various experiments performed concern both their structure and their kinetics of formation. The first deposit D1 has been used to determine by AES the evolution of the surface of the sample during annealing up to 680°C¹. The critical temperatures for Ni₃Al formation at the surface and Al dissolution in the bulk were consistent with the results obtained at the INSP. On sample B, a signal from Ni₃Al was always visible on the "clean sample" even after many cycles of sputtering. This was probably due to a high Al concentration near the surface due to the numerous deposits previously performed on sample B. On this sample we have undertaken preliminary tests of the Al₂O₃ formation by oxidation of Ni₃Al/Ni(111).

¹ the temperature given in this report is measured on the sample holder, and no correction is applied. At high temperature, it should be (previous calibration made by ID3 staff) slightly higher (by about 10°C) than the sample temperature.

Deposit #	Sample	Al quantity (ML)	Annealing temperature
1	A	3.3	progressively up to 680 °C
2		10	progressively up to 473 °C
3		7.5	11h at 300°C and by steps up to 430°C
4		+12.5	progressively up to 444°C
5		7.5	1.5h at 395°C
6		20	7h at 300° and by steps up to 520°C
7	B	2.5	15 min à 485°C
8		2.5	15 min at 465°C
9		5.3	20 min at 435°C

Table 1: Summary of the experiments performed on the kinetics of alloy formation. Deposit 7 has been performed during MDT (without X-rays).

I) Structure of the alloyed layers

a) lattice constant of Ni₃Al

No direct information on Al in substitution to Ni can be easily obtained since the lattice constant variation with Al concentration is very small (the Ni₃Al lattice constant is only 1% larger than the Ni lattice constant). We have determined that ordered Ni₃Al is in registry with Ni(111), with a small tetragonal distortion.

b) lattice constant of NiAl

The epitaxy of NiAl/Ni(111) is more complex (see fig. 1b). A distortion of the lattice constants with respect to NiAl is observed, which depends on the axis analysed. We have determined their evolution during annealing.

c) width of the spots

On the ordered alloys, we have measured after annealing the variation of the width of the diffraction spots along 3 orthogonal directions of the reciprocal space as function of the diffracted wave vector. This will allow us to determine the domain size and mosaicity, the variation of lattice constant and the nature of disorder inside the films.

II kinetics of formation of Ni₃Al and NiAl

During the various steps of our experiments, several original observations have been made which will be very enlightening for the complete understanding of the complex alloying path of the Al/Ni system.

1) During deposition, alloying already occurs at room temperature. Disordered NiAl (whose structure is very different from Ni-see Fig. 1 (b)) is observed by GIXD, whereas there is no evidence for the early formation of Ni₃Al (whose structure differs from that of Ni with substitutional Al atoms only by its chemical order-see section I(a)). Hence the presence of a disordered Ni₃Al alloyed film at the interface between Ni and NiAl is not excluded.

2) During annealing, in a first step, the NiAl layer grows up (the evolution can be reasonably followed in the 300°C-400°C temperature range). Simultaneously ordering of this layer occurs. We have always followed the evolution of different diffraction spots, characteristic of the ordered phase or not. During NiAl growth and ordering, a small diffraction signal from slightly ordered Ni₃Al can be detected at T higher than 350°C.

3) When the NiAl layer has grown up to the surface, ordered Ni₃Al begin to form. We simultaneously observe the decrease of the NiAl diffraction signal and the growth and sharpening of the diffraction spots characteristic of Ni₃Al.

4) Ni_3Al is stable up to 500°C . Annealing at higher temperature leads to the progressive dissolution of Al into the bulk. A thin Ni_3Al layer remains stable at the surface up to 560°C .

An additional observation is that a well-ordered Ni_3Al layer on Ni(111) is rapidly disordered under Al deposition at room temperature, with the simultaneous formation of disordered NiAl.

We presently undertake the detailed analysis of the thousand scans acquired in order to extract quantitative information on the diffusion and ordering (diffusion coefficient, activation energies...)

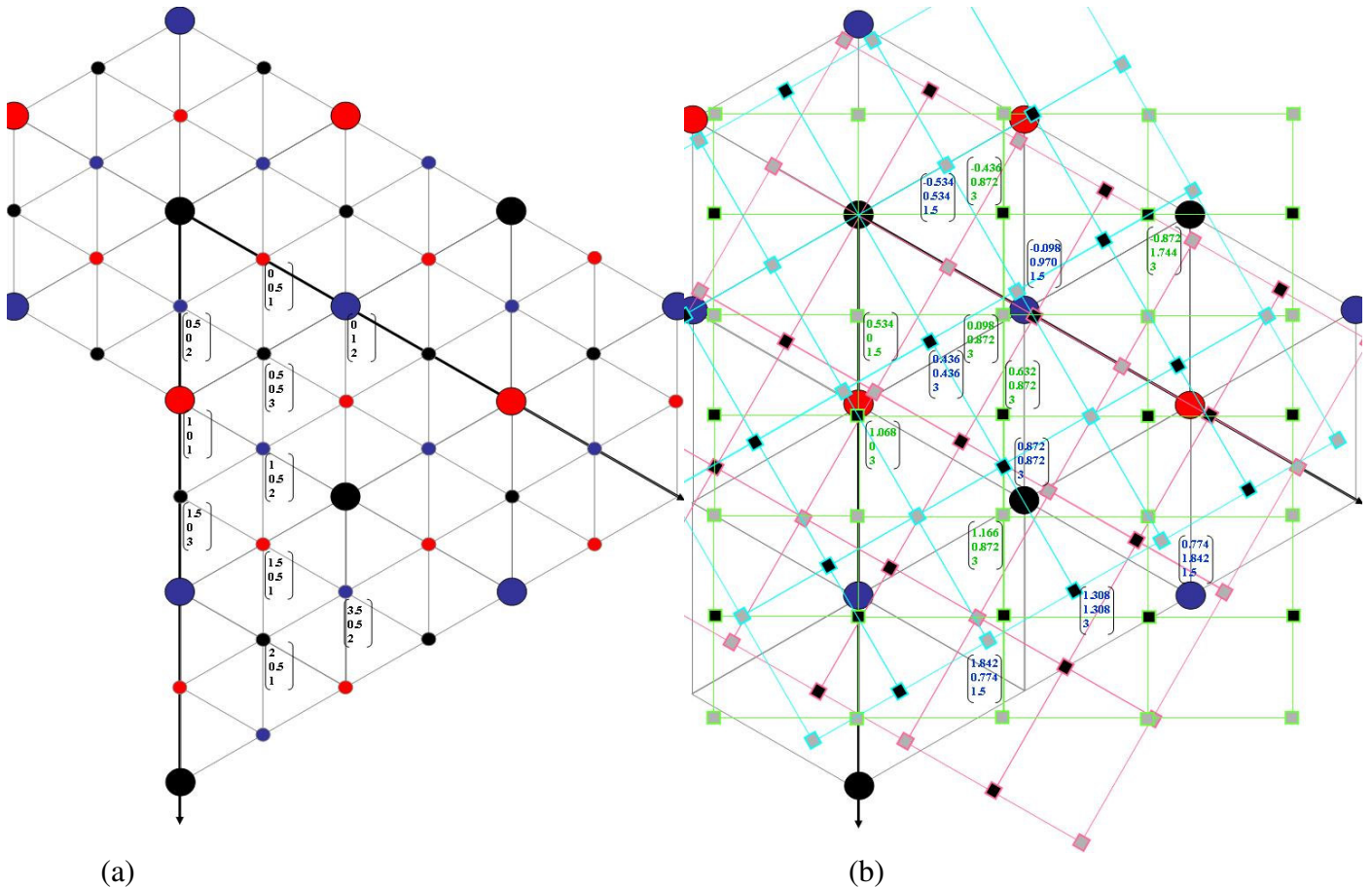


Figure 1. Reciprocal lattice of Ni_3Al (a) and NiAl (b) projected on the surface plane. Large dots refer to the Bragg spots of Ni. The symbol colors correspond to the L value of the Bragg spots. For Ni_3Al , the L value does not take into account the tetragonal distortion. For NiAl , the 3 variants are given, and their position is calculated accordingly to bulk NiAl .

III Alumina formation

We have oxidized the Ni_3Al layer formed after annealing of the Al deposit D9 (on sample B) by exposure to 1000 L O_2 at room temperature followed by annealing at 730°C . After annealing a well ordered $\text{Al}_2\text{O}_3/\text{Ni}(111)$ is formed, that can be observed by GIXD (see figure 2). The alumina layer adopts a $(5\sqrt{3}\times 5\sqrt{3})$ superstructure contracted by 2.5% with respect to the substrate. Since we have obtained the alumina layer in the last night of experiment, we have had only time for measuring few structure factors. This will be probably not sufficient for the determination of the whole structure, but it is very promising for future experiments.

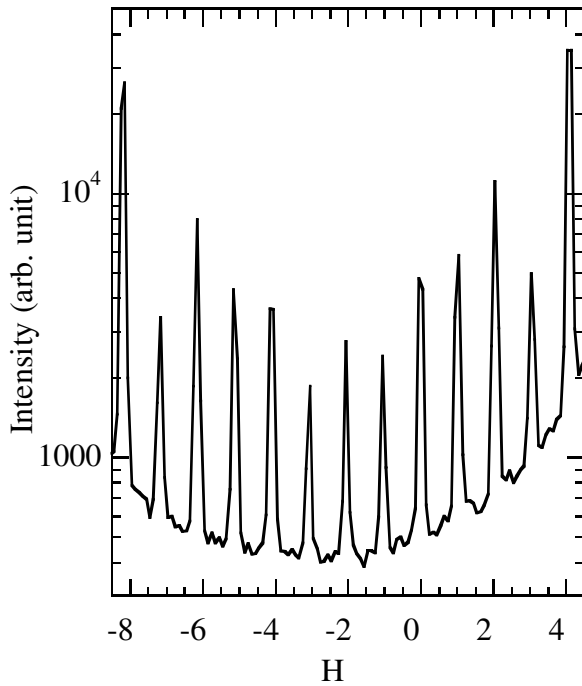


Figure 2: Diffracted intensity of the Al_2O_3 layer grown on $\text{Ni}(111)$ as a function of H for $K=4.1$ and $L=0.06$. The reciprocal lattice units are those corresponding to a $(5\sqrt{3}\times 5\sqrt{3})$ superstructure on the (111) surface of a fcc crystal.