

Growth of Ni–Al alloys on Ni(1 1 1), from Al deposits of various thicknesses: (II) Formation of NiAl over a Ni₃Al interfacial layer

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Abstract

This paper describes the second part of a study devoted to the growth of thin Ni–Al alloys after deposition of Al on Ni(1 1 1). In the previous paper [S. Le Pévédic, D. Schmaus, C. Cohen, Surf. Sci. 600 (2006) 565] we have described the results obtained for ultra-thin Al deposits, leading, after annealing at 750 K, to an epitaxial layer of Ni₃Al(1 1 1). In the present paper we show that this regime is only observed for Al deposits smaller than 8×10^{15} Al/cm² and we describe the results obtained for Al deposits exceeding this critical thickness, up to 200×10^{15} Al/cm². Al deposition was performed at low temperature (around 130 K) and the alloying process was followed in situ during subsequent annealing, by Auger electron spectroscopy, low energy electron diffraction and ion beam analysis-channeling measurements, in an ultra-high vacuum chamber connected to a Van de Graaff accelerator. We evidence the formation, after annealing at 750 K, of a crystallographically and chemically well-ordered NiAl(1 1 0) layer (whose thickness depends on the deposited Al amount), over a Ni₃Al “interfacial” layer (whose thickness—about 18 (1 1 1) planes—is independent of the deposited Al amount). The NiAl overlayer is composed of three variants, at 120° from each other in the surface plane, in relation with the respective symmetries of NiAl(1 1 0) and Ni₃Al(1 1 1). The NiAl layer is relaxed (the lattice parameters of cc-B2 NiAl and fcc-L1₂ Ni₃Al differ markedly), and we have determined its epitaxial relationship. In the case of the thickest alloyed layer formed the results concerning the structure of the NiAl layer have been confirmed and refined by ex situ X-ray diffraction and information on its grain size has been obtained by ex situ Atomic Force Microscopy. The kinetics of the alloying process is complex. It corresponds to an heterogeneous growth leading, above the thin Ni₃Al interfacial layer, to a mixture of Al and NiAl over the whole Al film, up to the surface. The atomic diffusion is very limited in the NiAl phase that forms, and thus the progressive enrichment in Ni of the Al film, i.e. of the mean Ni concentration, becomes slower and slower. As a consequence, alloying is observed to take place in a very broad temperature range between 300 K and 700 K. For annealing temperatures above 800 K, the alloyed layer is decomposed, Al atoms diffusing in the bulk of the substrate.

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1. Introduction

The study presented here concerns the growth of Ni–Al thin alloyed layers obtained from Al deposition on Ni(1 1 1). We have tried to answer the following question: what alloy is formed, and by what processes, as a function of the deposition and annealing temperatures and of the

deposited Al amount. Such a study presents a fundamental interest: can the alloyed layer formed be predicted from the equilibrium phase diagram established for bulk binary systems? What is the influence of the kinetics on this phase formation? From a more technological point of view, the great interest of Ni–Al alloys (in particular their resistance to corrosion at high temperature) has already been underlined in [1], where the first part of this study, devoted to ultra-thin Al deposits, has been presented. A key property of these alloys is the formation at their surface of a thin

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passive film of aluminum oxide. In particular the oxidation at high temperature of single crystals of Ni₃Al or NiAl ordered alloys (made possible by their high melting temperatures ($T_M(\text{Ni}_3\text{Al}) = 1658 \text{ K}$) and $T_M(\text{NiAl}) = 1911 \text{ K}$) leads to the formation of ultra-thin epitaxial layers of Al₂O₃ [2], impossible to obtain from an Al single crystal ($T_M(\text{Al}) = 933 \text{ K}$). An interest of such thin oxide films is that they can be easily studied without any problem of charge evacuation. Another interest is their use as model-supports for epitaxy of small metallic aggregates of interest

in catalysis [3]. They are also candidates for a possible use as insulating barriers in magnetic tunnel junctions [4].

In our previous paper [1], we have shown that ultra-thin Al deposits (below $8 \times 10^{15} \text{ Al/cm}^2$), achieved around 130 K, lead, after annealing around 750 K, to strained epitaxial Ni₃Al layers on top of Ni(111). We have also demonstrated that the $p(2 \times 2)$ structure observed on LEED patterns, which is characteristic of a crystallographically and chemically ordered Ni₃Al(111) surface, is not due to a surface Ni₃Al alloy. It is due to a three-dimensional

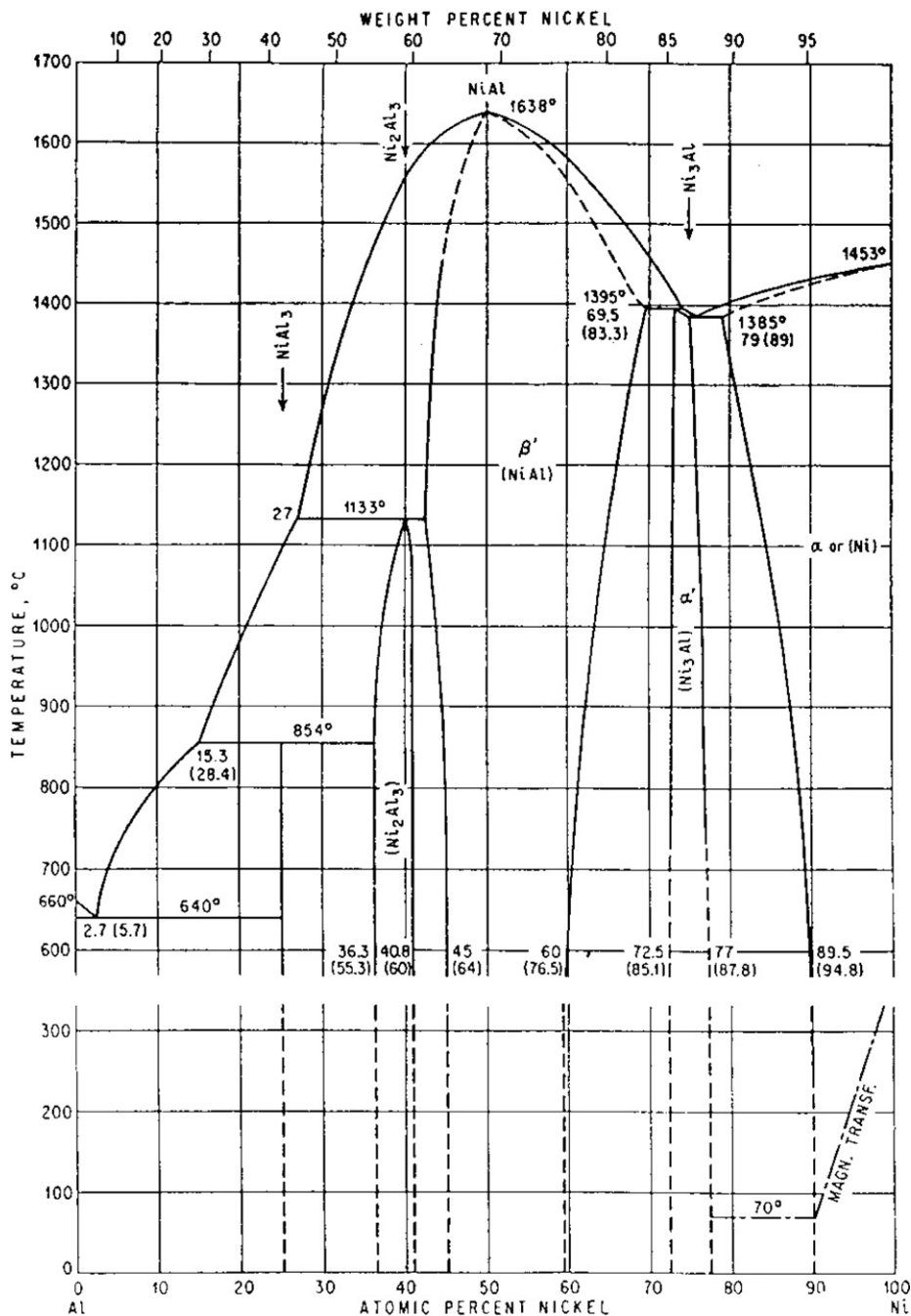


Fig. 1. Equilibrium bulk phase diagram of the binary Ni–Al system [5].

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