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PHASE TRANSFORMATIONS IN NICKEL-ALUMINUM ALLOYS DURING
ION BEAM MIXING*

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ABSTRACT

The effect of ion beam mixing of nickel-aluminum alloys with 500 keV krypton ions has been investigated over a range of temperature, composition, ion dose, and post-irradiation thermal treatments. Samples were formed by alternate evaporation of layers of aluminum and nickel. A portion of these samples was subsequently annealed to form intermetallic compounds. Irradiations were performed at both room temperature and 80 K using the 2 MV ion accelerator at Argonne National Laboratory. Phase transformations were observed during both in situ irradiations in the High Voltage Electron Microscope (HVEM) at Argonne and also in subsequent analysis of an array of irradiated samples. Electron diffraction indicates the presence of metastable crystalline structures not present in the conventional nickel-aluminum phase diagram. Transformations occur at doses as low as $5 \times 10^{14} \text{ cm}^{-2}$ and continue to develop as the irradiation progresses up to $2 \times 10^{16} \text{ cm}^{-2}$. Layer mixing is followed through Rutherford Backscattering analysis. Samples are also checked with x-rays and Electron Energy Loss Spectroscopy (EELS). A thermodynamic argument is presented to explain the phase transformations in terms of movements on a free energy diagram. This analysis explains the interesting paradox concerning the radiation hardness of the NiAl[1] phase and the amorphous structure of mixed Ni-50% Al layers[2].

INTRODUCTION

Ion beam mixing of thin layers offers a method of preparing alloys with unique structures. This is due to the thermodynamically non-equilibrium nature of the alloys so formed. This same attribute - metastability - can be found in structures formed by the irradiation of equilibrium alloys. These two processes can be followed on a thermodynamic free energy diagram as shown in Figure 1.

Several alloys become amorphous when irradiated with heavy ions[3]. It has been noted that mixing at liquid nitrogen temperature of Ni/Al layers in a composition of 50% produces an amorphous structure[2]. However, irradiation of the intermetallic bcc phase NiAl at the same temperature produces no such transformation. Presumably, this result could be explained by the alternate paths which each process must follow on the free energy diagram of Figure 1. If the free energy of the amorphous phase lies between that of the pure elements and that of the intermetallic NiAl, then it should be easier to reach that point by lowering the free energy of the layers during mixing, rather than by raising the free energy of the intermetallic.

In order to test this supposition, and to investigate various theories of phase formation during ion beam mixing, samples of Ni/Al alloys were prepared in various compositions as both annealed intermetallics and elemental layers, and irradiated with heavy ions over a range of doses at both room temperature and 80 K. These samples were examined in a transmission electron microscope and analyzed for phases present with electron diffraction.

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Schematic Free Energy Diagram

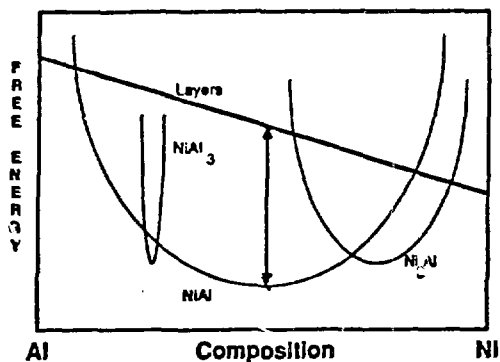


Figure 1. Schematic free energy diagram of the Ni/Al system showing energies of three intermetallic phases as well as the energy of a layered structure.

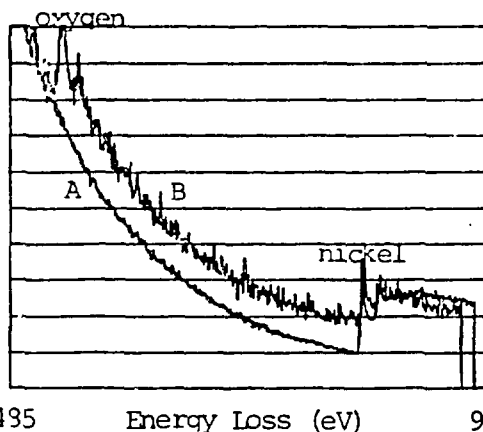


Figure 2. EELS plots showing the presence of oxygen in evaporated sample with outer Al layer (A), and lack of oxygen in similar sample with Ni outer layers (B).

EXPERIMENT

Samples were prepared by sequential electron-gun evaporation of nickel and aluminum layers on 300 mesh copper grids. This was done in a vacuum of better than 10^{-6} Torr. These grids were mounted in Crystalbond® and were soaked in acetone following evaporation to remove them from the mount. The resulting thin films smoothly spanned the holes in the mesh. All samples were prepared with nickel forming the outermost layers to impart oxidation resistance. The importance of this feature can be demonstrated by the EELS plot in Figure 2, which shows the presence of oxygen in a thin film in which aluminum forms the outermost layer, and the absence of oxygen in a similar film in which the aluminum is completely sandwiched between nickel layers. Despite the fact that some aluminum appears (from RBS) to migrate to the surface even in sandwiched samples, the nickel outer layers prevent the formation of any measurable oxidation. Impurities can have an important effect on the transformation kinetics and must therefore be carefully controlled.

Samples were prepared with three compositions corresponding to three intermetallics found in the Ni/Al phase diagram - $\text{NiAl}_3(\epsilon)$, $\text{NiAl}(\beta')$, and $\text{Ni}_3\text{Al}(\gamma')$. The NiAl samples were irradiated in the HVEM at Argonne National Laboratory. The other samples were irradiated in an ion pumped target chamber with a vacuum of better than 10^{-7} Torr at Argonne. Some samples were first annealed for 1 hour at 450°C in order to form the intermetallics mentioned previously. All samples were irradiated with 500 keV krypton ions which have a range of about 1200\AA , far exceeding the thickness of the films (about 750\AA). Doses ranged from $2 \times 10^{14} \text{ cm}^{-2}$ to $5 \times 10^{16} \text{ cm}^{-2}$, and samples were monitored during irradiation with an infrared monitor to ensure that no samples suffered irradiation heating exceeding the detection limit of the monitor, which is 100°C . Samples were analyzed using electron diffraction to identify phases. Mixing was monitored using Rutherford Backscattering performed with 1.8 MeV helium ions on layers prepared and irradiated on glass slides. There was some concern that mixing of the glass substrate into the surface layers would affect the nickel/aluminum mixing efficiency, but similar experiments performed using polished nickel substrates instead of glass have shown the same results.

RESULTS

NiAl₃

In all cases, samples of NiAl₃ composition formed an amorphous phase with some residual elemental aluminum. Intermetallic NiAl₃(ϵ) became amorphous at the lowest dose of $2 \times 10^{14} \text{ cm}^{-2}$, while the layers needed to be mixed to a dose of $2 \times 10^{16} \text{ cm}^{-2}$ before the amorphous phase appeared. At lower doses, the layered structure underwent different transformations at room temperature than at 80 K. At 80 K, the diffraction pattern indicated a smooth transition from elemental aluminum and nickel to less elemental aluminum and amorphous with increasing dose. At room temperature, the intermetallic NiAl formed at the lowest dose. As the mixing proceeded up to $1 \times 10^{16} \text{ cm}^{-2}$, the β' rings faded and disappeared and a new ring appeared at a lattice spacing of 1.26 \AA and grew in intensity. Then, between 1 and $2 \times 10^{16} \text{ cm}^{-2}$, the sample became amorphous with a residual amount of crystalline aluminum. The phase transformation can be followed in Figure 3, while the RBS spectra showing the mixing can be seen in Figure 4. The mixing of the layers is not complete, even at the high dose of $5 \times 10^{16} \text{ cm}^{-2}$.

Ni₃Al

The intermetallic phase Ni₃Al(γ') irradiated at 80 K showed the simplest response, merely becoming disordered at $2 \times 10^{14} \text{ cm}^{-2}$ and remaining disordered up to $2 \times 10^{16} \text{ cm}^{-2}$. The other three structures, including the layers irradiated at both room temperature and 80 K, and the γ' sample irradiated at room temperature, showed more interesting behavior. In all cases, the β' phase formed at low doses, and disappeared after a dose of $1 \times 10^{16} \text{ cm}^{-2}$ was reached. At this point, a very strong ring appeared at 2.21 \AA , along with several fainter rings. The lattice spacings of the faint rings vary with each set of samples, but the strong ring at 2.21 \AA is common to all three structures. This lattice spacing is not found in any Ni/Al intermetallic. In order to check for possible contamination as a cause of this strong ring, a mixed sample was annealed in a hot stage in a STEM at 400°C for 1/2 hour. The sample quickly reverted to a Ni₃Al ordered structure and the 2.21 \AA ring faded. This sequence of transformations is shown in Figure 5, along with a sequence of RBS spectra in Figure 6 showing the extent of mixing at different doses.

NiAl

Intermetallic NiAl(β') showed only some incomplete disordering after receiving a dose of $1 \times 10^{16} \text{ cm}^{-2}$ at -140°C . The Ni/Al layers irradiated at this temperature and composition showed more interesting behavior. The initial Ni/Al rings faded quickly, and at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ the diffraction pattern showed an amorphous ring centered about 2.0 \AA . As the irradiation progressed, this hazy ring proceeded to sharpen, and other rings began to appear. At a dose of $2 \times 10^{16} \text{ cm}^{-2}$, the amorphous ring was gone and a pattern showing disordered β' was present.

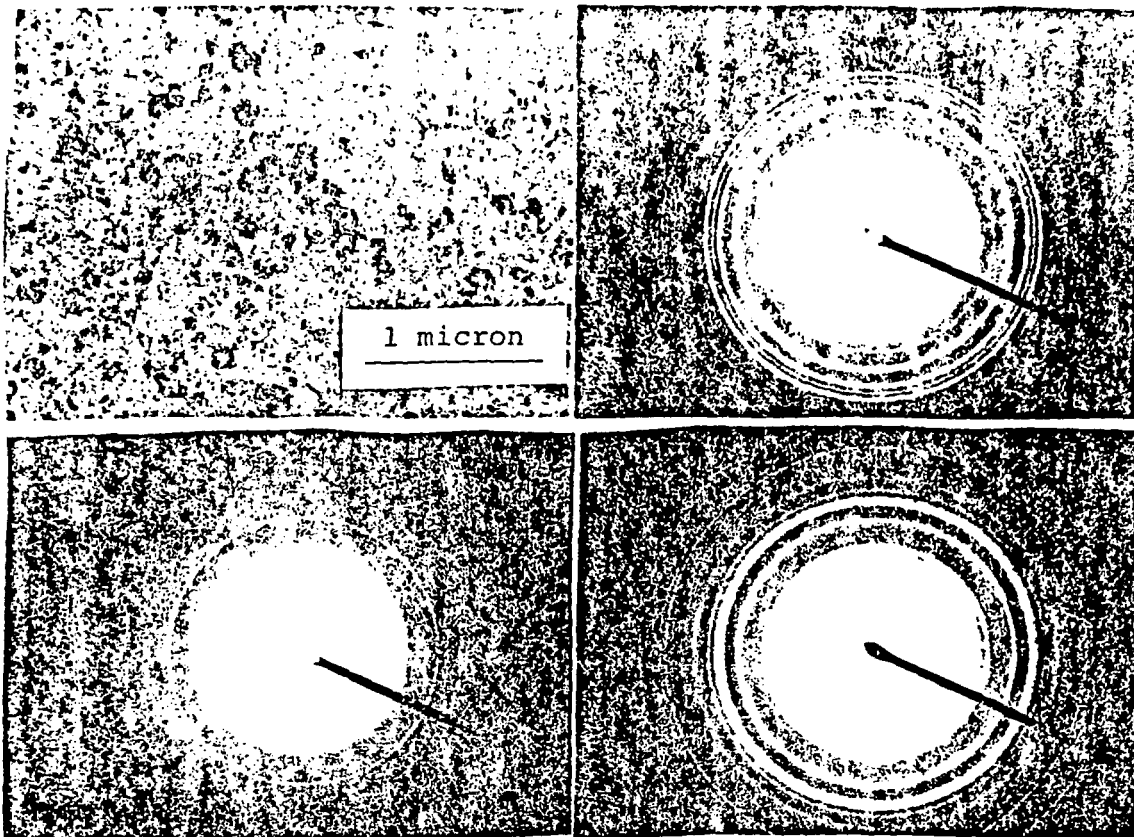


Figure 3. Micrograph and diffraction patterns from Ni-75%Al layers irradiated at room temperature showing (clockwise from upper left) initial evaporated fine grained structure; Al and NiAl rings formed at $2 \times 10^{15} / \text{cm}^2$; Al rings and unknown bright ring at 1.26 Å formed at $1 \times 10^{16} / \text{cm}^2$; Al rings and amorphous halo formed after mixing to 5×10^{16} .

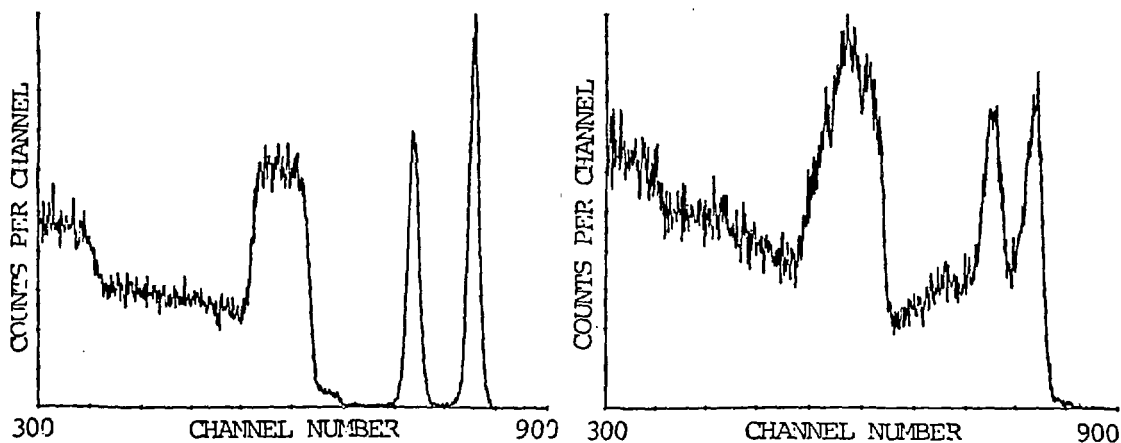


Figure 4. Rutherford Backscattering spectra showing initial layered structure of Ni-75%Al samples (left) and the same sample following mixing to a dose of 5×10^{16} ions/ cm^2 . Notice that the mixing is not complete.

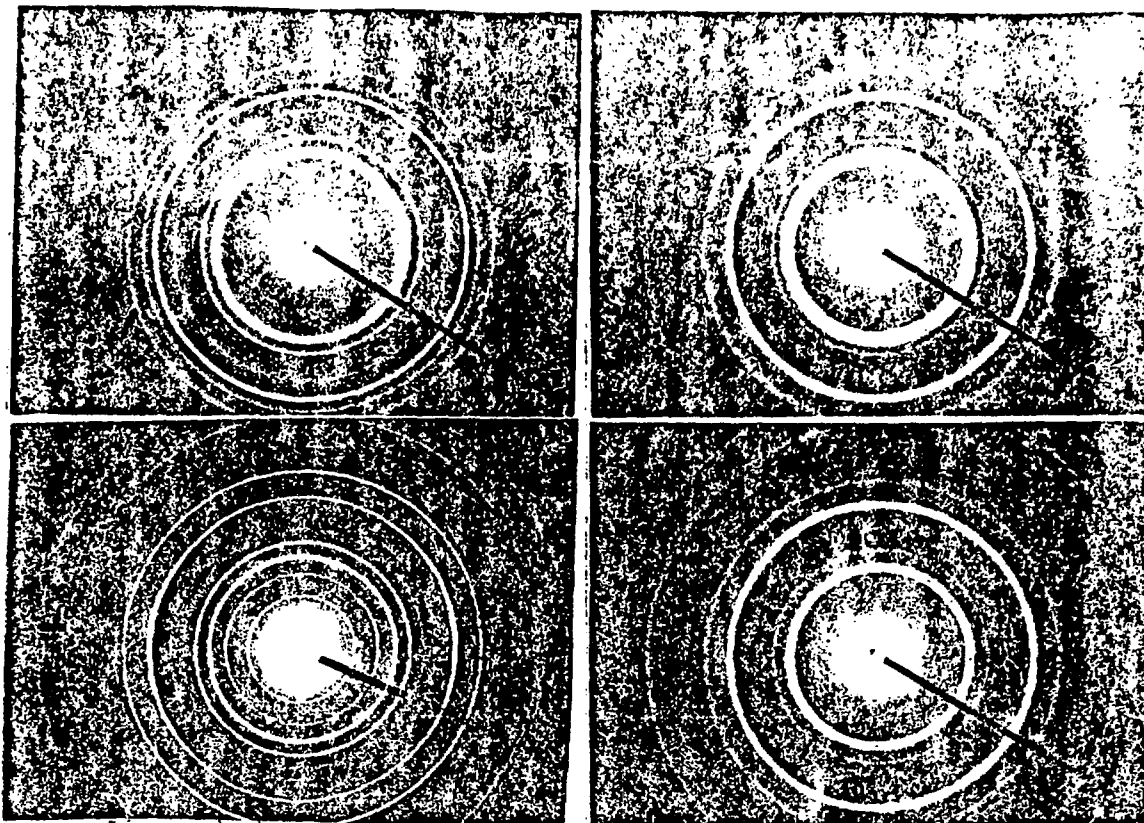


Figure 5. Sequence of diffraction patterns from Ni-25%Al layers irradiated at room temperature showing (clockwise from upper left) Ni and NiAl rings at 2×10^{15} ions/cm²; Ni rings and two bright unknown rings around the Ni (111) ring at 1×10^{16} ; Ni rings and a bright unknown ring at 2.21 Å; ordered Ni₃Al rings formed following annealing at 400 C for 1 hour.

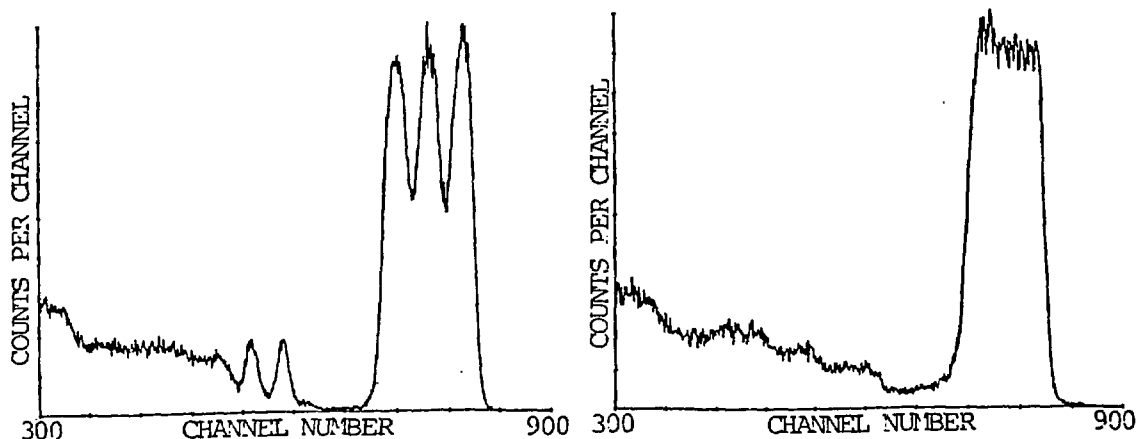


Figure 6. Rutherford Backscattering spectra showing initial layered structure of Ni-25%Al samples (left) and the same sample following mixing to a dose of 2×10^{16} ions/cm². Notice that the mixing is complete.

DISCUSSION

When considering what phases will form during ion beam mixing of metal layers, thermodynamics will determine which phases are most likely, and kinetics will determine which ones will actually form. In the Ni/Al system, β' is the most stable intermetallic with a heat of formation of 13 kcal/g-atom, compared with 9 and 10 kcal/g-atom for ϵ and γ' , respectively[4]. During mixing, β' frequently forms at low and intermediate ($0.5-5 \times 10^{15} \text{ cm}^{-2}$) doses, probably in the region near the interface of the Ni/Al layers. As the mixing proceeds and the sample becomes more homogeneous, the β' becomes less favorable energetically than other phases, such as the amorphous phase at aluminum-rich concentrations, and disordered γ' at nickel rich concentrations. Apparently, there is yet another structure, as yet unidentified, which is energetically favored in the irradiation environment at a composition of Ni-25%Al and which has a lattice plane spacing of 2.21Å in some direction. This phase can be formed at 80 K by mixing layers, but not by irradiation of the intermetallic γ' at this temperature. This illustrates the important interplay between thermodynamics and kinetics in determining phase formation. As the layers are mixed, the sample lowers its free energy and the new phase is inevitably favored energetically and may form even with the limited kinetics available at 80 K. The intermetallic γ' must, on the other hand, rise in free energy and re-order itself, and this cannot be done at 80 K, although it is possible at room temperature.

An interesting question raised by this work is the precise structure of the high dose Ni₃Al samples. The intensity of the 2.21Å ring indicates a large diffracting volume, while the absence of an entire set of new rings may mean that the new ring is the result of a minor modification of the basic fcc lattice. The reversibility of the transition back to γ' upon annealing indicates that it is not the result of an oxide or some other impurity. The further investigation of this structure should prove interesting.

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