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METASTABLE PHASE FORMATION IN NICKEL-ALUMINUM ALLOYS
DURING ION BEAM MIXING*

James Eridon**, Lynn Rehn and Gary Was**

Materials Science Division
Argonne National Laboratory
Argonne, Illinois 60439

**The University of Michigan, Ann Arbor, MI 48109

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METASTABLE PHASE FORMATION IN NICKEL-ALUMINUM ALLOYS DURING ION BEAM MIXING

JAMES ERIDON*, LYNN REHN**, AND GARY WAS*

*University of Michigan, Dept. of Nuclear Engineering, Ann Arbor, Michigan 48109

**Argonne National Laboratory, Materials Science and Technology Division, Argonne,
Illinois 60439

Abstract

Phase transformations induced by ion beam mixing of nickel-aluminum alloys with 500 keV krypton ions have been investigated over a range of temperatures, compositions, and initial structures. Samples were formed by alternate evaporation of layers of nickel and aluminum. 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 at Argonne and also in subsequent electron diffraction analysis of an array of irradiated samples. Metastable phases formed include disordered crystalline structures, an amorphous structure, and a hexagonal close-packed structure. These phase structures were modeled using the embedded atom method to compute energies of transition from stable to metastable states. The effects of both thermodynamics and kinetics on metastable phase formation are evaluated.

1. Introduction

Ion beam mixing of thin layers offers a method of preparing alloys with unique structures. This is due to the thermodynamic non-equilibrium nature of the alloys so formed. This same attribute – metastability – can be found in structures formed by the irradiation of equilibrium alloys. There are three basic types of metastable alloys which may be formed through heavy ion irradiation of crystalline structures: amorphous phases with no long range order, crystalline phases with structures different from that of the stable intermetallic alloy, and 'disordered' crystalline phases with structures based on the same lattice as that of the stable intermetallic.

Several empirical rules have been offered to predict when a given intermetallic alloy should become amorphous under irradiation such as the structural difference rule, the complex structure rule[1], the ratio of atomic radii rule[2], and the range of homogeneity rule[3]. The experimental data contain exceptions to all of these rules. Furthermore, none of these rules addresses the formation of metastable crystalline phases. The purpose of this work is to examine one particular alloy system, the nickel-aluminum system, in detail in regards to the formation of metastable crystalline and amorphous alloys through heavy ion irradiation. This will be accomplished through irradiation of samples of various compositions and computer modeling of the thermodynamic properties of the metastable alloys formed through the irradiation. The goal is to provide an explanation of the observed phenomena in the nickel-aluminum system as well as a deeper appreciation of the aforementioned empirical rules – why they apply in general but fail in a few particular cases.

2. Experimental Procedure and Results

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. The 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. It has been found through Electron Energy Loss Spectroscopy (EELS) of evaporated thin films that when aluminum forms the outer layer in a nickel-aluminum sample, appreciable oxidation of the surface occurs following a brief exposure to the atmosphere[4]. No such oxidation is apparent in samples in which nickel forms the outermost layer. This is an important consideration since impurities can significantly affect the transformation kinetics.

Samples were prepared with three compositions corresponding to three intermetallics found in the Ni/Al phase diagram – NiAl₃(ϵ), NiAl(β'), and Ni₃Al(γ'). The sample set was split in two, with one half remaining layered while the other half was annealed for one hour at 723 K in order to form the intermetallic phases mentioned previously. Some equiatomic NiAl samples were irradiated in the HVEM at Argonne National Laboratory (ANL). All other samples were irradiated in an ion pumped target chamber with a vacuum of better than 10^{-7} Torr at ANL. Half the samples were irradiated at room temperature, while the other half were irradiated at 80 K in sample holders cooled with liquid nitrogen. All samples were irradiated with 500 keV krypton ions which have a range of about 1200Å, well beyond the thickness of the films (about 750Å). 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 surface heating exceeding the 373 K detection limit of the monitor. 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[4].

2.1 $NiAl_3$

In all cases, samples of $NiAl_3$ composition formed an amorphous phase with some residual elemental aluminum. Intermetallic $NiAl_3(\epsilon)$ 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 a two-phase structure containing an amorphous phase and elemental aluminum. At room temperature, the intermetallic $NiAl(\beta')$ formed at the lowest dose. As the mixing proceeded up to $1 \times 10^{16} \text{ cm}^{-2}$, the β' rings faded and a new ring appeared at a lattice spacing of 1.26 \AA and grew in intensity. Between 1×10^{16} and $2 \times 10^{16} \text{ cm}^{-2}$ the sample became amorphous with a residual amount of crystalline aluminum. Annealing of samples containing this amorphous phase produced rapid crystallization (in less than 10 seconds) at a temperature of about 500 K. The diffraction patterns from an amorphous sample and the same sample following annealing to form the intermetallic ϵ phase are shown in figure 1.

2.2 Ni_3Al

The intermetallic phase $Ni_3Al(\gamma')$ 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 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 2.20 \AA , along with several fainter rings. This 2.20 \AA ring is the $\{100\}$ reflection of an ideally close-packed hexagonal structure with the same nearest neighbor distance as the disordered fcc structure of γ' . This hcp structure forms with a very strong texture; the basal planes of the hexagonal prisms are all aligned parallel to the plane of the foil, so that the $[001]$ direction is parallel to the direction of the incoming ions ($[001]$ is a channeling direction in the hcp lattice). This texture is shown in

figure 2, in which the {101} hcp ring is not apparent in the electron diffraction pattern taken at 0° tilt, but appears at 30° tilt in a direction perpendicular to the tilt axis. Upon annealing, this hcp structure disappears and ordered γ' forms, as shown in figure 2. This annealing step is not as rapid as that which occurs in NiAl₃. It occurs over the course of about one hour at 673 K.

2.3 NiAl

Intermetallic NiAl(β') showed only partial disordering after receiving a dose of $1 \times 10^{16} \text{ cm}^{-2}$ at 133 K in the HVEM cold stage. The Ni/Al layers irradiated under the same conditions showed more interesting behavior. The initial nickel and aluminum rings faded quickly, and at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ the diffraction pattern showed an amorphous ring centered at about 2.0Å. 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. This mixing experiment was repeated in the target chamber at 80 K with the same results. In similar work done by Jaouen et.al.[5], the formation of the amorphous phase has been reported, but not the subsequent recrystallization as disordered β' upon further irradiation. This may be due to the relatively low doses ($7 \times 10^{15} \text{ cm}^{-2}$ of 340 kV xenon ions) used in this investigation. Irradiation of layers of this composition at room temperature resulted in the formation of ordered β' . The amorphous diffraction pattern formed at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ and the crystalline pattern formed at $2 \times 10^{16} \text{ cm}^{-2}$ are shown in figure 3.

3. Thermodynamic Modeling of Stable and Metastable Phases

The thermodynamic parameter of greatest interest in describing the metastable phases produced in this experiment is the heat of formation, ΔH_f . This value has been measured experimentally for the stable intermetallic phases[6], but must be calculated for the metastable phases. In this work, the embedded atom model developed by Daw and Baskes[7] was used. Details on the application of this model to the nickel-aluminum alloy system may be found elsewhere[4].

Using this model, the heats of formation of both ordered and disordered γ' , β' , and ϵ were computed in order to examine the relative magnitude of the energy change associated with the formation of these disordered phases. Note, however, that disordered ϵ (NiAl_3) was never formed. Instead, an amorphous phase was created at this composition. Thus, some model of this amorphous structure is needed.

The amorphous NiAl_3 phase was modeled by displacing atoms from their equilibrium positions in the crystalline D0_{20} lattice in random directions by an amount between 0 and $\pm 0.200 \text{ \AA}$. The resulting pair distribution function of this structure is shown in figure 4. This function is characteristic of an amorphous structure in several ways. First, there is a tendency toward a nearly constant value of unity at large radii, indicating the loss of long range order. Also, the relative locations of the first three peaks are characteristic of amorphous metals[8]. This shows a relatively high degree of similarity between complex structures and amorphous structures. A pair distribution function based on the B2 lattice of NiAl (β'), computed using the same random atom displacement method applied to NiAl_3 , is also shown in figure 4. This function shows much less amorphous character, indicating a much larger difference between the B2 structure and an amorphous structure.

With this model, the results in Table 1 were calculated, which show the heat of formation ΔH_f for various stable and metastable phases, as well as the difference between the heat of formation of the stable and metastable phases at each given composition, ΔH_{s-ms} . As expected, ΔH_{s-ms} is positive in all cases, indicating that all phases formed through ion irradiation are indeed metastable. This fact is confirmed by the behavior of these phases upon annealing, where all metastable phases recrystallize in the stable states. Interestingly, the disordered γ' phase and the hexagonal close packed phase at the 25%aluminum composition have almost exactly the same energy. This might be expected, since both structures are close packed and have identical numbers of first and second nearest neighbors at the same radii, although in a somewhat different configuration. This energy is also

the same amount necessary to disorder β' , but the energy necessary to disorder ϵ is over two and a half times as large. On the other hand, the energy necessary to amorphize NiAl_3 is much smaller (nearly five times) than the disordering energy of the intermetallic compound.

4. 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, the metastable phases which form under ion irradiation all have computed heats of formation of less than 7.3 kJ/g-atom, while the one phase which conspicuously does not form, disordered NiAl_3 (ϵ), has a heat of formation over twice this value. Furthermore, two metastable crystalline structures can be created at a composition of 25%aluminum, with nearly identical energies of formation. This demonstrates the importance of thermodynamics in determining metastable phase formation.

The importance of kinetics is demonstrated in two cases. At equiatomic composition, it is possible to form disordered β' by mixing layers at 133 K, but not by irradiating the ordered compound. In this latter case, forming a disordered structure requires an increase in the energy of the ordered alloy, while in the former, it entails a decrease in energy of the nickel and aluminum layers. The path of decreasing free energy leads to the formation of the disordered alloy.

At 25%aluminum composition, it is possible to form the hcp phase by irradiating the ordered γ' alloy at room temperature, but this phase does not form when the ordered alloy is irradiated at 80 K. Although, energetically, both the disordered fcc and hcp phases are equally probable, the atomic re-arrangement necessary to produce the hcp phase cannot proceed with the limited kinetics available at 80 K. However, when Ni/Al layers of this composition are irradiated at 80 K, the kinetics are improved through the addition of the heat of mixing of pure nickel and aluminum, and the hcp phase is allowed to form.

All the empirical rules mentioned in the introduction are indirectly related to these two simple criteria, thermodynamics and kinetics. The empirical rules which attempt to predict amorphous phase formation are actually predictions of the magnitude of ΔH_{s-ms} . For example, complex structures require relatively small structural modifications to make them appear amorphous, and therefore little energy change should be associated with this transformation. Similarly, an intermetallic alloy with a broad range of homogeneity might be expected to be greatly lower in free energy than any competing crystal structure, while one with a very narrow homogeneity range might be near in energy to a competing (perhaps amorphous) structure. This may explain, for example, why a simple alloy such as NiTi (cubic B2 structure, 1% homogeneity range) amorphizes easily under irradiation, in violation of the complex structure rule but in accordance with the range of homogeneity rule. Because these rules are empirical predictions, and not actual measurements or calculations of ΔH_{s-ms} , they will occasionally fail, as in the case of Ni_3Ti , an alloy with no range of homogeneity which steadfastly remains crystalline under 2.5 MeV nickel ion bombardment[3].

In summary, the results from the nickel-aluminum system indicate that the formation of metastable phases through ion irradiation can be explained on the basis of thermodynamics and kinetics. The existing empirical rules of amorphous phase formation are indirectly related to thermodynamics, but express the same ideas. The application of thermodynamic modeling to other systems to predict metastable phase formation should prove interesting.

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References

- [1] L.S. Hung, M. Nastasi, J. Gyulai, J.W. Mayer, *Applied Physics Letters* 42 (1983) 672.
- [2] S. Mader, *Journal of Vacuum Science and Technology* 2 (1965) 35.
- [3] J.L. Brimhall, H.E. Kissinger, L.A. Charlot, *Radiation Effects*, 77 (1983) 273.
- [4] J. Eridon, Ph.D. Dissertation, University of Michigan, (1986).
- [5] C. Jaouen, J.P. Riviere, A. Bellara, J. Delafond, *Nuclear Instruments and Methods* B7/8 (1985) 591.
- [6] R. Hultgren, P. Desai, D. Hawkins, M. Gleiser, and K. Kelly, *Selected Values of the Thermodynamic Properties of Binary Alloys* (Am. Soc. Metals, 1973).
- [7] M.S. Daw, M.I. Baskes, *Physical Review B* 29 (1984) 6443.
- [8] Y. Waseda, H. Okazaki, T. Masumoto, *Journal of Materials Science* 12 (1977) 1927.

LIST OF FIGURES

- Figure 1. Electron diffraction patterns from Ni-75% Al samples. Left: amorphous pattern from annealed sample (ϵ -phase) irradiated at 80 K. Right: same sample following annealing at 503 K for 1 minute. Note the rapid recrystallization.
- Figure 2. Electron diffraction patterns from Ni-25% Al samples. Clockwise from top: dual phase pattern showing disordered γ and hcp phase arising after irradiation of annealed sample (γ -phase) at 300 K to a dose of $2 \times 10^{16} \text{ cm}^{-2}$ with 500 keV krypton ions; sample viewed at 30° tilt, showing the appearance of $\{101\}$ hcp ring indicating texture; similar sample following annealing at 673 K for 1 hour, showing the appearance of ordered γ superlattice rings.
- Figure 3. Electron diffraction patterns from Ni-50% Al samples. Clockwise from top: rings arising from elemental aluminum and nickel in a layered sample before irradiation; similar sample following irradiation to a dose of $2 \times 10^{15} \text{ cm}^{-2}$ at 80 K showing some amorphous character; similar sample following irradiation to a dose of $2 \times 10^{16} \text{ cm}^{-2}$, showing pattern from disordered β' .
- Figure 4. Pair distribution functions arising from NiAl_3 (top) and NiAl (bottom) following a computer modeled "amorphization" process. Note the amorphous character of the NiAl_3 plot, which indicates how close the DO_{20} structure is to an amorphous structure.

TABLE 1

Composition	Structure	ΔH_f (kJ)	ΔH_{s-ms} (kJ)
Ni-75%Al	D0 ₂₀ (ord)	-37.6	stable
	D0 ₂₀ (dis)	-18.4	19.2
	amorphous	-33.8	3.9
Ni-50%Al	B2 (ord)	-58.8	stable
	B2 (dis)	-51.5	7.2
Ni-25%Al	L1 ₂ (ord)	-38.7	stable
	L1 ₂ (dis)	-31.5	7.2
	A3 (dis)	-31.4	7.3

Table 1. Heat of formation ΔH_f and heat of stable-metastable transition ΔH_{s-ms} for various stable and metastable structures in the nickel-aluminum alloy system. All energies are in units of 10^3 Joule, (ord)=ordered, (dis)=disordered.

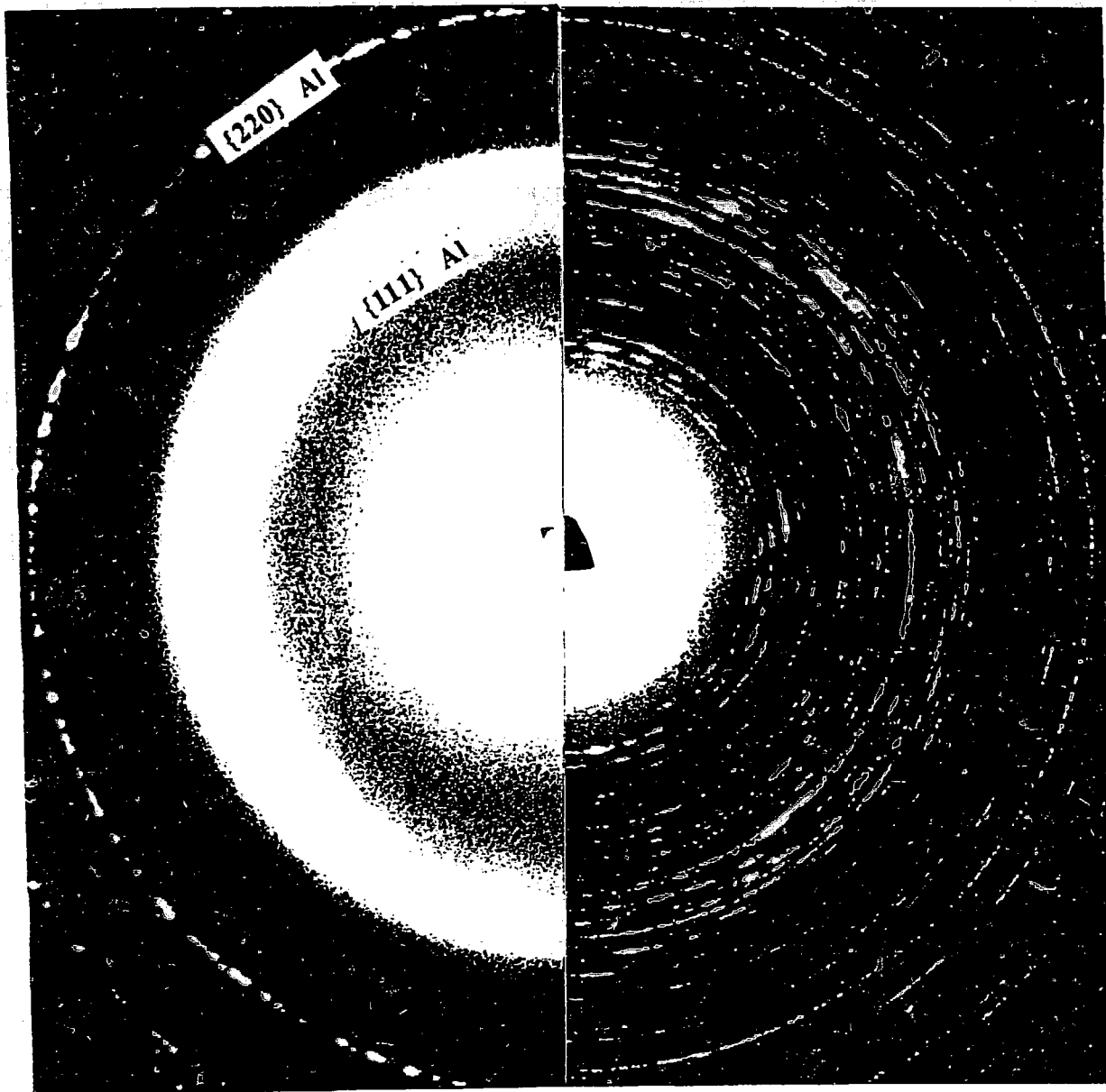


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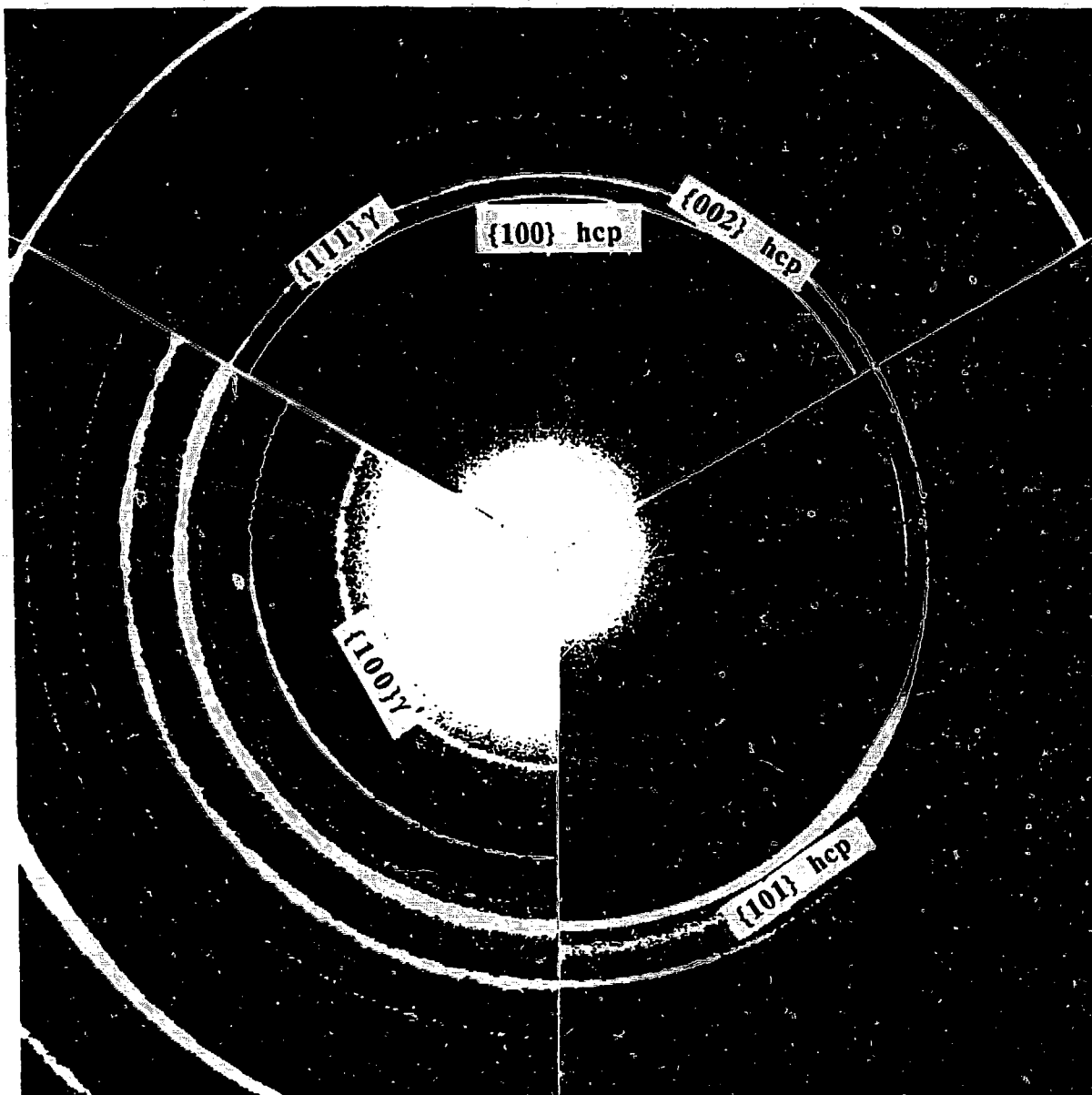


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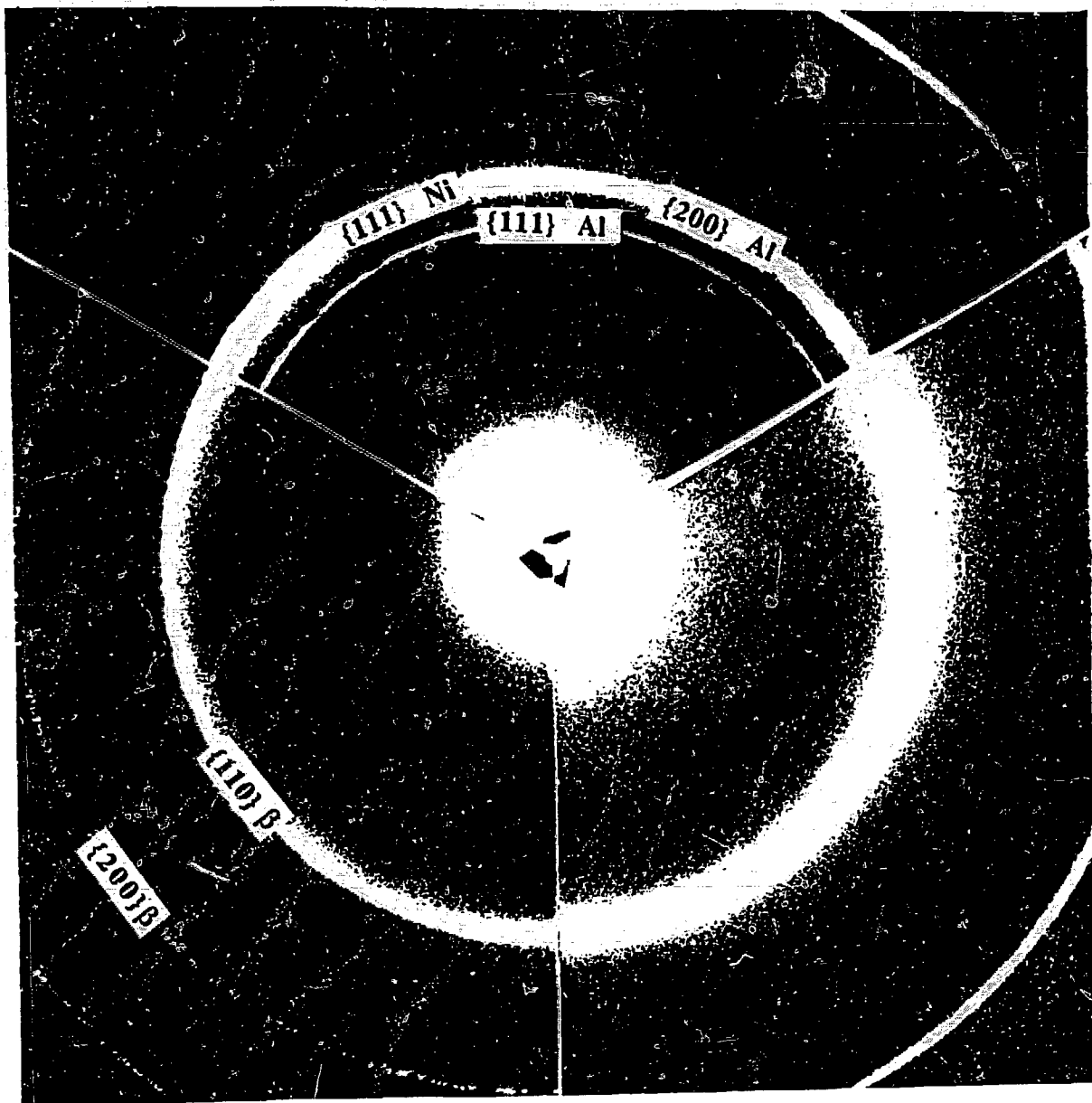


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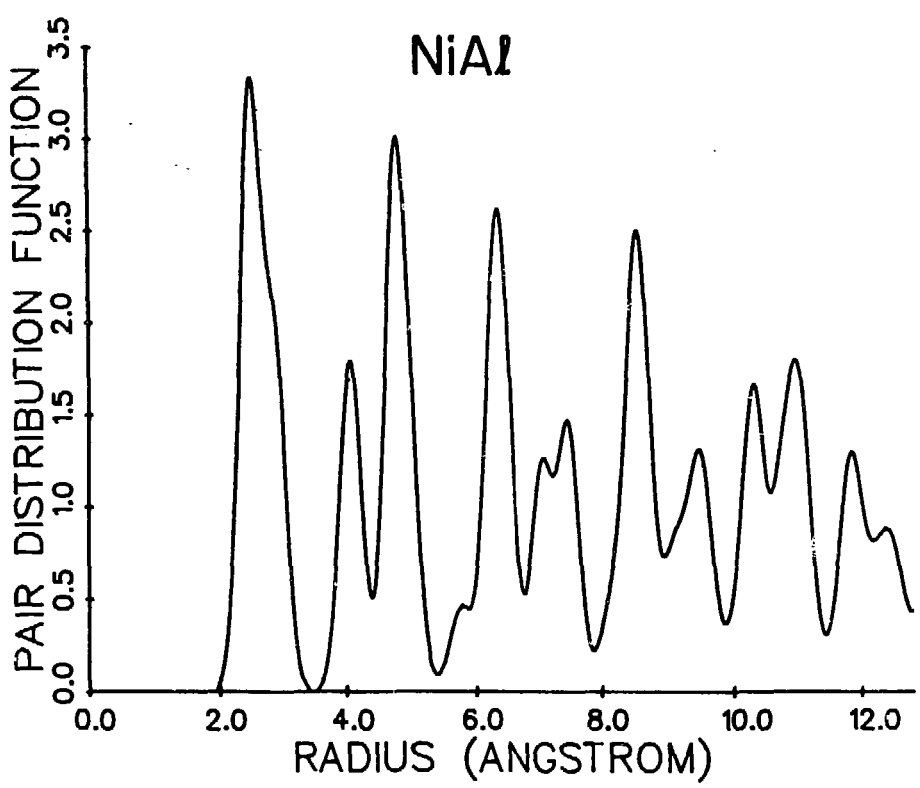
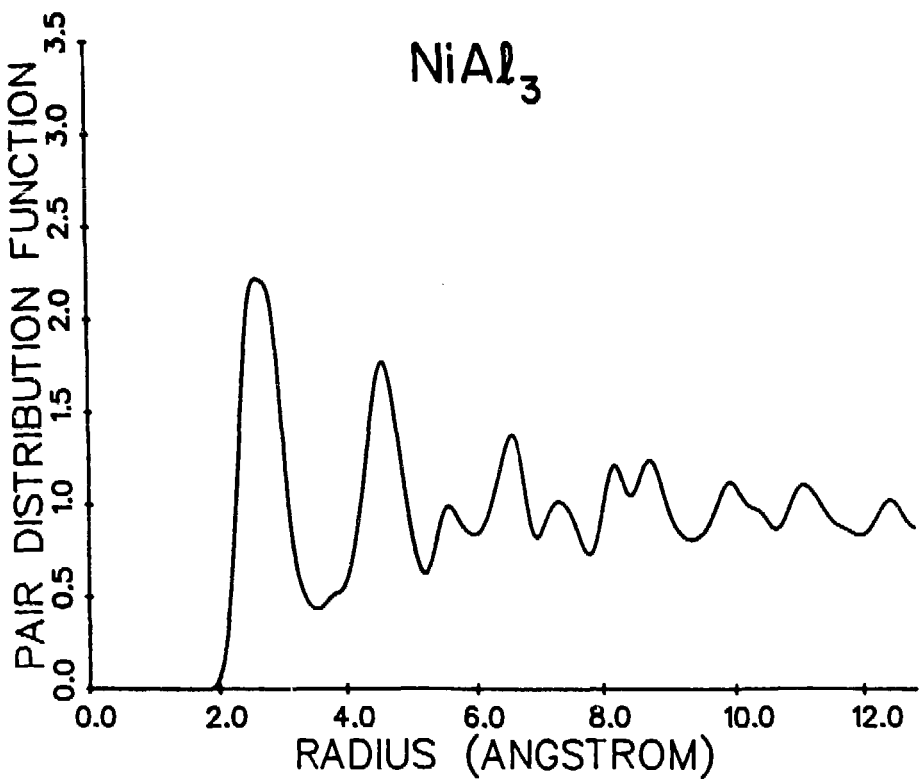


Figure 4. Pair distribution functions arising from NiAl_3 (top) and NiAl (bottom) following a computer modeled "amorphization" process. Note the amorphous character of the NiAl_3 plot, which indicates how close the D0_{20} structure is to an amorphous structure.