

tials more positive than  $-0.4$  V vs SCE on ZnO under irradiation, while it was observed at the potentials more positive than  $+0.6$  V vs SCE on SnO<sub>2</sub>. Therefore, photoelectrochemical polymerization proceeds selectively on ZnO when the potential of the photoetched substrate electrode is set between  $-0.4$  and  $+0.6$  V vs SCE. On the other hand, in the dark, no anodic current appeared up to  $+1.5$  V vs SCE on ZnO while it was observed at potentials more positive than  $+0.6$  V vs SCE. Therefore, electrochemical polymerization proceeds selectively on SnO<sub>2</sub> when the potential of the photoetched substrate electrode is set between  $+0.6$  and  $+1.5$  V vs SCE. Thus, prepared polypyrrole patterns on ZnO and on SnO<sub>2</sub> are shown in Figs. 5(a) and 5(b), respectively.

In the latter two procedures of area-selective deposition, ZnO is working as an inorganic photoresist material. ZnO has a very fascinating peculiarity as a photoresist that it can be removed in neutral aqueous solution by irradiation. This is an important characteristic because application of functional organic materials and biological elements into devices in the future needs fabrication of them under mild conditions.

In conclusion, area-selective deposition of polypyrrole was successfully performed by three different procedures in polypyrrole-ZnO system with electrochemical and photoelectrochemical techniques. These methods are important as

tools for fabrication of organic devices (including conducting pattern generation) and functionalization of electrode surfaces, which is essential for fabrication of chemical- and biosensors.

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## Dual phase formation in multilayered Ni-Al by ion beam mixing

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Ion beam mixing is used to homogenize multilayered thin films of nickel and aluminum, vapor deposited onto pure nickel substrates. Doses of 500-keV Kr<sup>+</sup> at fluences of  $2 \times 10^{16}$  ions/cm<sup>2</sup> produced a supersaturated solid solution of between 16 and 23 at. % aluminum in nickel at room temperature. Subsequent thermal treatment at 425 °C for 1 h resulted in the formation of a dual phase structure of  $\gamma$  and  $\gamma'$  with grain sizes in the range 640 to 710 Å. Although the dual phase structure was obtained either by ion beam mixing followed by thermal annealing or by thermal annealing alone, only the former process resulted in a surface film with a texture. The films are stable against thermally induced grain growth at temperatures up to 700 °C for 10 h.

Ion beam mixing has been used to induce phase transformations in a wide variety of alloy systems.<sup>1-4</sup> Tsaur *et al.*<sup>1</sup> investigated ion-induced atomic mixing with Xe<sup>+</sup> as an alternate approach to conventional rapid quenching techniques for producing thin-film metastable alloys. They

found that the formation of metastable phases such as supersaturated solid solutions or amorphous alloys can be obtained as a result of atomic mixing. Post-irradiation heat treatment of the atomically mixed binary alloy usually results in a decomposition to the equilibrium structure.

In this work, we are interested in the ion beam induced phase transformations of layers of Ni-(16-23 at. %)Al, va-

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por deposited onto pure Ni substrates. The ultimate goal of this work is the delay of fatigue crack initiation in polycrystalline nickel samples that have undergone surface modification by ion beam mixing of a multilayered structure of Ni and Al. The presence of a surface layer of  $\gamma + \gamma'$  on a Ni ( $\gamma$ ) substrate is expected to significantly alter the fatigue crack initiation process.<sup>5</sup> Potter, Ahmed, and Lamond<sup>2</sup> found that such a structure could be created by the implantation of Al into Ni in the temperature range 300–600 °C in agreement with the equilibrium phase diagram. However, implantation at room temperature showed no evidence of the  $\gamma'$  phase in specimens implanted up to 25 at. % Al. It is our objective to

determine if a  $\gamma/\gamma'$  surface layer can be produced with ion beam mixing, and if so, what degree of control this process affords.

Substrates of large grain ( $>100 \mu\text{m}$ ) polycrystalline Ni were mechanically and electrochemically polished to produce a surface finish with a roughness better than 500 Å. Upon each substrate, five layers (3 nickel sandwiching 2 aluminum) were deposited at room temperature by electron-gun evaporation to a total thickness of  $\sim 600 \text{ \AA}$ . The individual layer thicknesses were controlled to yield an overall composition between 16 and 23 at. % Al. Rutherford backscattering spectrometry (RBS) was conducted using

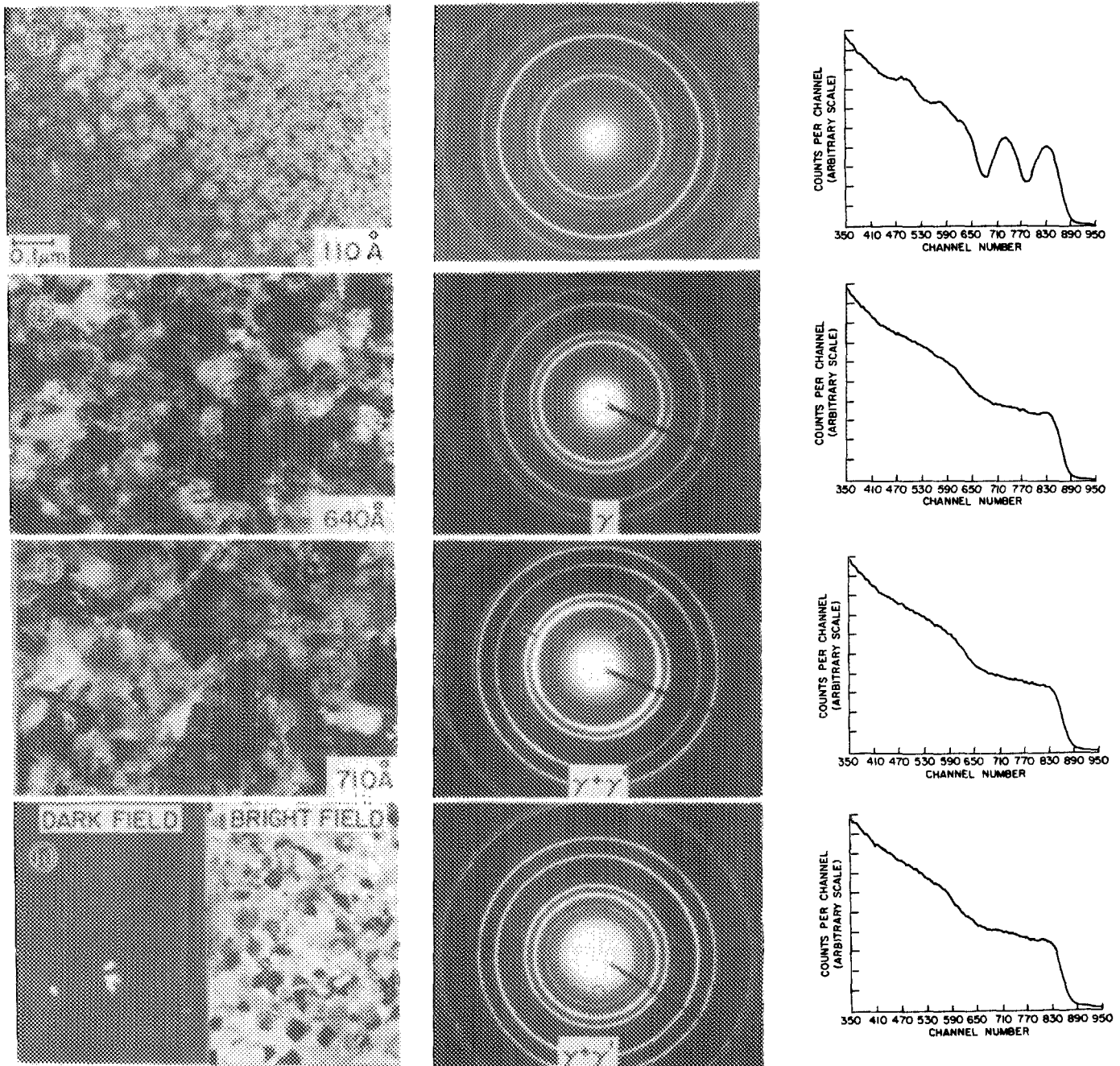


FIG. 1. Characterization by transmission electron microscopy, electron diffraction, and Rutherford backscattering spectrometry of (a) as-evaporated layers of composition Ni-16% Al, (b) layers mixed at room temperature with 500-keV  $\text{Kr}^+$  to  $2 \times 10^{16}$  ions/cm<sup>2</sup>, (c) ion beam mixed structure heated at 425 °C for 1 h and (d) as-evaporated layers heated at 425 °C for 1 h.

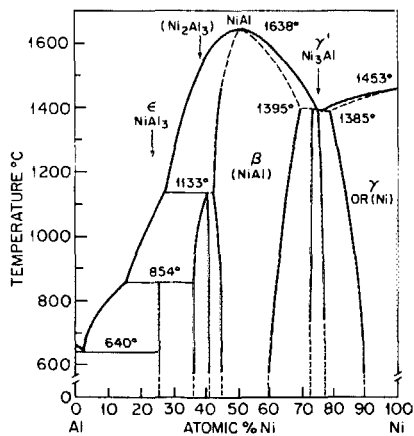


FIG. 2. The equilibrium phase diagram for bulk alloys of the nickel-aluminum system (Ref. 7).

the 2-MV tandem accelerator at Argonne National Laboratory. The spectra were analyzed to determine the depth versus concentration profile using the computer code BASF.<sup>6</sup> After verification of the composition of the surface layer, samples were irradiated at room temperature with a 500-keV  $\text{Kr}^+$  beam to a dose of  $2 \times 10^{16}$  ions/cm<sup>2</sup>. RBS was again performed, followed by a thermal anneal on selected samples.

Evaporation of Ni and Al onto Ni substrates at room temperature resulted in very fine grains ( $\sim 110$  Å) of the deposited metals. The raw RBS spectrum, electron diffraction pattern, and TEM image from the as-deposited layers are shown in Fig. 1(a). Ion beam mixing with 500-keV  $\text{Kr}^+$  to  $2 \times 10^{16}$  ions/cm<sup>2</sup> resulted in substantial homogenization of the surface layer and grain growth to  $\sim 640$  Å [Fig. 1(b)]. Electron diffraction reveals the presence of only the  $\gamma$  phase, although the surface layer composition is clearly within the two phase  $\gamma + \gamma'$  region of the equilibrium phase diagram (Fig. 2). These results are in agreement with those of Potter, Ahmed, and Lamond,<sup>2</sup> who showed that direct implantation of Al into Ni at room temperature resulted only in the  $\gamma$  phase.

However, upon subsequent heating at 425 °C for 1 h, the  $\gamma$  structure decomposed into a two phase  $\gamma + \gamma'$  structure, as shown in Fig. 1(c). Note first that there is little change in the RBS spectrum, indicating that minimal thermal mixing has occurred. This is in agreement with measurements of grain size which show an increase of only  $\sim 10\%$ , from 640 to 710 Å. However, the striking feature of the resulting structure is that it is both dual phase and textured. That is, the grains are partitioned into  $\gamma$  grains and  $\gamma'$  grains as opposed to a distribution of  $\gamma'$  precipitates in a  $\gamma$  matrix, and these  $\gamma'$  grains have grown with a preferred orientation. The texture is indicated in Fig. 1(c) by the arrows on the (110), (111), and (220) rings. This texture is probably dependent on the presence of the substrate, since Cu-Ag layers evaporated onto sapphire substrates showed no sign of texture after a similar sequence of ion beam and thermal treatments.<sup>8</sup> While the actual volume fraction of  $\gamma'$  is a quantity of interest, it is difficult to evaluate due to the small grain size.

Layered samples heated without ion beam mixing, [Fig. 1(d)], showed a similar distribution of  $\gamma$  and  $\gamma'$  but with no texture and only minimal grain growth. The dual phase na-

ture of the surface is indicated by the bright-field/dark-field pair in which the dark-field image was taken using a (100) diffraction spot. This dual phase structure is the same as that seen in the irradiated sample.

Grain growth occurs predominantly during the ion beam mixing step. An increase in grain size by a factor of six was observed after a dose of  $1 \times 10^{16}$  ions/cm<sup>2</sup> on the multilayered sample. Thermal treatments applied either before or after mixing produced only minimal grain growth (a factor of 1.1 to 1.4) for temperatures up to 700 °C for 10 h. Hence, the fine grain structure is quite stable against thermally induced growth. Oxidation was a continual problem during annealing and often occurred preferentially in the ion beam mixed region of the samples.

Although ion beam mixing of Ni-Al layers followed by thermal treatment produces the intended  $\gamma/\gamma'$  layer, its character is substantially different from that achieved through either conventional processing or direct implantation of Al into Ni. Potter, Ahmed, and Lamond demonstrated that implantation of Al into Ni at 300–600 °C to a level between 10 and 23 at. % results in  $\gamma'$  in a  $\gamma$  solid solution in agreement with the equilibrium phase diagram.<sup>2</sup> They also found that implantation at room temperature produced only a supersaturated solid solution—in agreement with our ion beam mixing experiments. Both sets of results support the known disordering reaction of the  $\text{L1}_2$  structure under low-temperature irradiation.<sup>2,9–11</sup> However, while remaining disordered, substantial growth of the Ni-Al grains (up to the thickness of the deposited layers  $\sim 600$  Å) occurred as also observed by Tsaur *et al.* in Au-Ni.<sup>1</sup> The ordering which occurs during subsequent thermal annealing is a result of structure relaxation due to enhanced atomic migration. Although it is somewhat puzzling why a dual phase structure should form during thermal treatment, this structure poses a unique and as yet unanalyzed case for fatigue crack initiation studies.

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