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Non-equilibrium intermixing and phase transformation in severely deformed Al/Ni multilayers

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Al/Ni multilayers were prepared by repeated folding and cold rolling (F&R) of elemental foils. The thickness of Al and Ni foils was reduced down to less than 50 nm after 50 F&R cycles. Three-dimensional atom probe analyses clearly reveal the presence of supersaturated solid solutions and provide evidence of deformation-induced intermixing. The formation of the solid solutions and their transformation into the Al_3Ni phase upon annealing is discussed.

Keywords: Rolling; Multilayers; Nickel aluminides; Three-dimensional atom probe; Nanocrystalline

Phase transformations in thin metallic multilayer systems have been extensively investigated. During heating of multiphase structures synthesized in thin multilayers, stable or metastable intermediate phases may appear as a result of interdiffusion and subsequent phase transformations. Apart from "static" microstructure features, interdiffusion or intermixing prior to phase transformation, and associated concentration gradients, play a key role in determining the phase formation kinetics [1,2]. It is well known that severe plastic deformation can induce significant mixing, as in ball-milled powders [3–7]. Similar features have also been reported for torsion under high pressure [8] and cold rolling [9]. Since this latter technique is also suitable for the preparation of metallic multilayers [9–12], it was used to prepare Al/Ni multilayers to clarify the influence of concentration gradients and the intermixing state on the phase transformation kinetics upon annealing. The Al–Ni system was chosen as a model system since it is both attractive for applications, e.g. in superalloys or as coatings of III–V semiconductors, and has also been studied thoroughly concerning the microstructure and phase evolution [10,11,13–21]. In the studies reported so far, thin Al/Ni multilayers have mostly been deposited by sputtering [17,19,20] or electron-beam evaporation [16,19–21], while repeated folding and cold rolling (F&R) of Al and Ni foils was also applied as an alternative process to synthesize Al/Ni multilayer foils [10–12,14,18]. By this method, layers with thicknesses in the nanometer range were obtained and it was shown that such samples exhibit very similar phase transformation sequences and almost identical kinetic behaviour upon annealing compared to thin film multilayers that had been synthesized by deposition methods [12]. Yet, in the literature, different phase formation sequences have been reported for different nominal compositions and after different processing pathways. Under most conditions, the Al_3Ni phase with an ordered $D0_{20}$ structure is the first phase to form. This is explained by the asymmetry of the interdiffusion coefficients, with Ni diffusing much more rapidly into Al than Al into Ni [22,23]. However, depending on the nominal composition of the multilayer and on the processing history, different initial intermediate phases such as AlNi [19,20,24–26], $AlNi_3$ [10] or a metastable Al_9Ni_2-phase [24,27] were also observed. In this context, it is interesting to analyse whether the phase formation sequence is

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determined by the processing route, and especially by the presence of concentration gradients prior to annealing. Three-dimensional atom probe (3D-AP) analyses were performed to map out these concentration gradients at the atomic scale on F&R-processed multilayers prior to and after thermal annealing. In particular, we have investigated how local modifications of the distribution of constituents and the presence of steep concentration profiles can change the kinetics of intermediate phase formation.

Al/Ni multilayer samples of nominal composition $Al_{80}Ni_{20}$ were prepared from high-purity foils of Ni (99.9%, 20 μm thick) and Al (99.9%, 100 μm thick) that were alternately stacked to form a 20 mm × 20 mm and 500 μm thick sandwich. This sample was then cold rolled (roll diameter 150 mm, 2 rotations per minute) to a thickness of 200 μm in 10 passes, then folded to double the thickness and rolled again to a thickness of 200 μm. This procedure was repeated 50 times. The final material was investigated in the as-prepared state and after brief annealing in a differential scanning calorimeter (DSC, Pyris 1, Perkin Elmer) under flowing argon for 2 min at 250 °C. This temperature was chosen because it is close to the onset of Al_3Ni formation [12,14,17,18], and the duration was sufficiently short to avoid significant grain growth. Phase identification was carried out using X-ray diffraction (XRD, Phillips X'Pert) with a Cu anode source operating at 50 kV and 40 mA. The microstructure of the multilayer was examined in a FEI/Tecnai F20 ST transmission electron microscope (TEM) operating at 200 kV with an extraction voltage for the field-emission gun of 4.1 kV, using a Philips double-tilt holder. TEM samples were prepared in cross-section geometry by ion milling using a Gatan Precision Ion Polishing System (PIPS 691) operating at 3.5 kV with an angle of incidence of 4°. 3D-AP analyses were performed with a CAMECA tomographic atom probe detection system (TAP) and analyses were carried out at 80 K with a pulse fraction of 16% in UHV conditions. 3D-AP samples were prepared by electropolishing (20 °C, 10 V, 2% perchloric acid in 2-butoxyethanol).

During the cold-rolling process, both Al and Ni foils are severely elongated in the rolling plane, resulting in a multilayer system with layer thickness in the nanometer range as indicated in Figure 1. The average thickness of the layers is about 10–50 nm after 50 F&R cycles. XRD data indicate that only the face-centered cubic (fcc) Al and fcc Ni phases are present in the as-rolled multilayers, indicating further that no detectable phase formation reaction between Al and Ni occurred during the repeated deformation process (Fig. 2).

Some pure Ni and pure Al regions were analysed by 3D-AP (not shown), but a significant intermixing of Al and Ni was also revealed (Fig. 3). Regions containing between 15 at.% Ni and even up to 60 at.% Ni were indeed detected, especially where the layer thickness was in the range of 10 nm or less (measured by field ion microscopy prior to 3D-AP analysis). Since both XRD and selected area electron diffraction in the TEM revealed only fcc Al and fcc Ni in the as-prepared sample, these mixed regions are attributed to metastable or – for the highest Ni content – even non-equilibrium supersaturated solid solutions. It is important to note

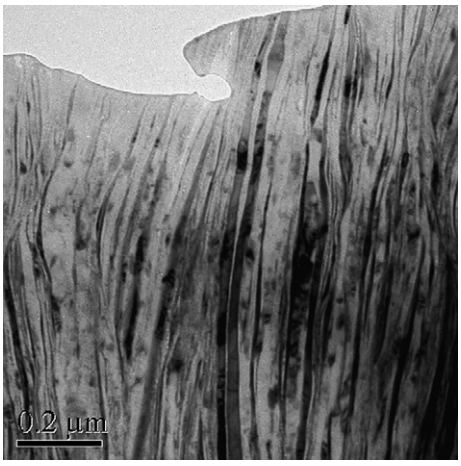

Figure 1. TEM bright-field image showing the cross-sectional microstructure of the cold-rolled Al/Ni multilayer.

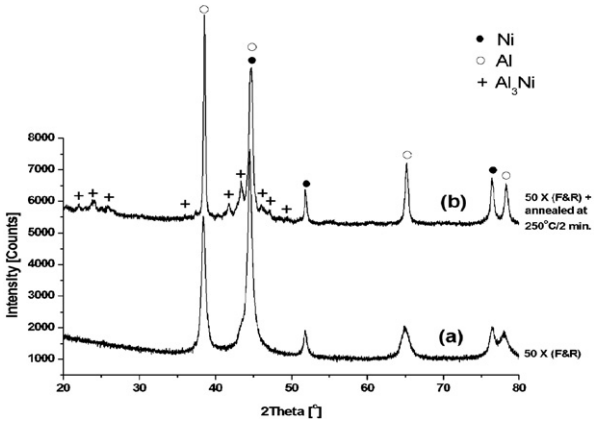

Figure 2. X-ray diffraction results of the Al/Ni multilayer in the as-prepared state and after brief annealing, which causes the formation of the Al_3Ni phase as indicated by the additional Bragg reflections.

that no impurity was detected on mass spectra, indicating that there was no contamination during the F&R process. Up to now it has been reported that cold-rolled multilayers exhibit sharp interfaces [10–12,12,16], e.g. without significant mixing like deposited or sputtered multilayers [19,20]. However, in these earlier studies of F&R multilayers the local distribution of the constituents was not checked at the atomic scale. On the other hand, the formation of supersaturated solid solutions by ball milling was reported for Al–Ni powders [5,28], and for many different systems [6,7]. In the present case, it seems clear from the composition distribution in Figure 3 that the mixing process is controlled by the diffusion of Ni in Al in agreement with ball-milling data [5]. From the composition profile of Figure 3, the effective diffusion distance R^* is estimated to be about 10 nm. Then, considering the roll geometry and the roll velocity, the total deformation time is $\tau_d \approx 30$ s. This yields an effective diffusion coefficient $D^* = R^{*2}/\tau_d = 1/3 \times 10^{-18}$ m^2 s^{-1}. Extrapolation of experimental thermal diffusion data shows that similar values are measured at temperatures above 600 K [29]. Such a temperature increase is unrealistic because of the low