Experimental evidence for the role of supersaturated interfacial alloys on the shear elastic softening of Ni/Mo superlattices

G. Abadias,[1,*] C. Jaouen,[1] F. Martin,[1] J. Pacaud,[1] Ph. Djemia,[2] and F. Ganot[2]
[1]*Laboratoire de Métallurgie Physique, UMR CNRS 6630, Université de Poitiers, SP2MI, Téléport 2, BP 30179, 86962 Futuroscope-Chasseneuil Cedex, France*
[2]*Laboratoire des Propriétés Mécaniques et Thermodynamiques des Matériaux, UPR CNRS 9001, Université Paris Nord, Avenue J.B. Clément, 93430 Villetaneuse, France*
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The importance of the interfaces in governing the elastic behavior of nanometer-scale metallic superlattices has long been recognized, although their intrinsic nature and the underlying physical mechanisms are still subject to controversy. In the present study, the key role of an interfacial alloying effect on the dramatic softening (-62%) in the shear elastic constant C_{44} of Ni/Mo multilayers is clearly evidenced. By combining x-ray diffraction and Brillouin light scattering experiments on both Ni/Mo superlattices and $Ni_{1-x}Mo_x$ solid solution samples, we show that the formation of metastable alloys, obtained either by cosputtering or stabilized at the interfaces, induces an elastic lattice instability. In addition, the extremely low value of C_{44} observed for the multilayers, at small modulation periods, suggests the stabilization under epitaxial growth of a highly supersaturated interfacial alloyed layer.

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The presence in some multilayers systems of deviations in the elastic behavior compared with that predicted by the continuum elasticity, so-called elastic ''anomalies,'' has given rise to the development of both considerable experimental and theoretical studies in the past ten years, in order to determine the underlying mechanisms responsible for these peculiar physical properties.[1] Strong hardenings involving an increase of the in-plane biaxial modulus by more than 100%, referred as a ''supermodulus'' effect,[2] have been originally evidenced in some fcc/fcc systems from bulge-tester techniques. Although after reexamination this effect has been denied, it is now well established that significant elastic anomalies do exist for some peculiar bcc/fcc systems [e.g., Cu/Nb (Ref. 3), W/Ni (Ref. 4), and Mo/Ni (Refs. 5–7)] and less frequently for fcc/fcc ones [e.g., Ag/Ni (Ref. 8)]: a drastic softening ($\sim 30\%-50\%$) in shear elastic moduli is observed as the bilayer period (Λ) decreases.

It has been shown that the softening of the shear and compressional moduli is directly correlated with the expansion of the average lattice spacing along the growth direction ($\bar{d}$) and also possibly to an increased structural disorder near the interfaces able to drive a crystalline-to-amorphous transition at small Λ.[4] Different models[1] involving either a bulk lattice deformation (due to a modified electronic band structure) or a localized strain (due to interface stresses), or even a model based on the concept of ''grain boundary'' interfaces and related atomic-level disorder,[9] have been proposed. Despite a considerable effort, the issue of the elastic properties of metallic superlattices is not yet well elucidated.

These conflicting results have led us to reconsider the Ni/Mo system, for which the elastic anomaly is one of the most pronounced among those of the metallic binary systems reported in the literature.[1] By carrying out a detailed structural study coupled with Brillouin light scattering (BLS) measurements on both Ni/Mo multilayers and $Ni_{1-x}Mo_x$ solid solution samples, we show that the formation of supersaturated metastable alloys, obtained either by cosputtering or stabilized at the interfaces, induces a strong elastic softening of the shear modulus. The present experimental results bring not only a clear evidence of the prime role of the interfaces in governing the elastic behavior of metallic superlattices, but also permit us to specify the underlying mechanism, i.e., an alloying-induced elastic lattice instability.

Ni/Mo multilayered (with Λ ranging from 16 to 1000 Å) and $Ni_{1-x}Mo_x$ solid solutions (in the entire composition range) samples were elaborated at room temperature (RT) using a high-vacuum (base pressure $\leqslant 10^{-8}$ Torr) sputtering apparatus equipped with a RF-plasma ion gun. They were grown on natural-oxydized (001) Si substrates using a 1.2-kV accelerated Ar ion beam and with a deposition rate lower than 1 Å/s. The Ni/Mo thickness ratio of the multilayers corresponds to a global composition of $x_{Mo}=0.25 \pm 0.02$, as measured by energy-dispersive x-ray spectroscopy. The total thickness of the multilayers always amounts to $\sim$2800 Å, and the solid solutions one is $\sim$2000 Å.

X-ray diffraction (XRD) experiments performed in the θ-2θ Bragg-Brentano geometry reveal at high angles the presence of sharp and intense diffraction peaks.[10] This indicates the existence of crystalline interfaces with no coherency loss, even at very small Λ ($<$20 Å) where amorphous structures have often been observed.[4,6] A strong crystalline texture within the constituent layers is found in all samples, the (111) fcc planes of the Ni layers being parallel with the (110) bcc planes of the Mo layers. The high-angle XRD spectra were fitted using the SUPREX program[11] until a consistent solution was found for both first- and second-order peaks. This procedure allows us to obtain accurate values of the average lattice spacing of the individual Mo and Ni layers, respectively, d_{Mo} and d_{Ni}. The value of $\bar{d}$ is measured directly from the main Bragg peak position. A relative expansion of $\bar{d}$ of $\sim 1\%$ is found in the whole range of the

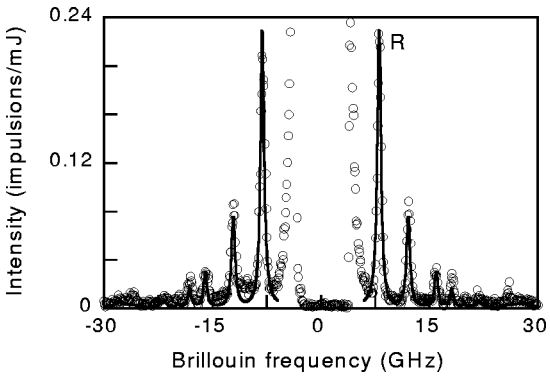

FIG. 1. Typical experimental Brillouin spectrum (dots) compared with the calculated one (line) for a Ni/Mo multilayer with $\Lambda = 75$ Å. The Rayleigh surface mode (noted *R*) is fitted with $C_{44} = 48$ GPa ($C_{11} = 310$ GPa, $C_{33} = 370$ GPa, $C_{13} = 151$ GPa allow a convenient fit of the other modes).

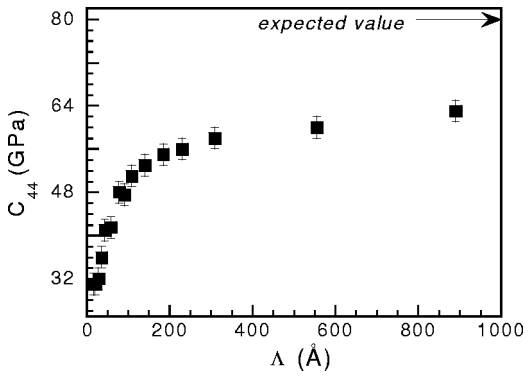

FIG. 2. Effective elastic constant C_{44} (determined from BLS) vs Λ for the multilayers samples. The arrow indicates the expected value (Hill average): 80 GPa.

investigated Λ.[10] This suggests that the layers are under a global compressive stress state.

BLS measurements were used to determine the phase velocity of the surface acoustic phonons for both the multilayers and solid solution samples. The spectra were recorded in air at RT on a high-contrast Sandercok-type 3+3 pass tandem Fabry-Perot interferometer with use of ~400 mW of $\lambda = 5145$ Å radiation from a single-moded Ar^+ laser in the backscattering configuration. Since the phonons acoustic wavelength (typically 300 nm) is larger than the Λ values investigated, the elastic properties of the multilayers can be described within the elastic continuum approximation. The set of elastic constants was determined by fitting the Brillouin spectra (see Fig. 1) for different angles of incidence of the laser beam, assuming that the ripple mechanism at the free surface[12] is the only efficient one. Total thickness and density (ρ) required for the calculation were obtained from x-ray reflectometry. In the present case of hexagonal effective symmetry, among the five independent constants, only C_{11}, C_{33}, C_{13}, and C_{44} are related to the observed Brillouin spectra lines. Nevertheless, an unambiguous determination is only possible for C_{44}.[8] In fact, for layer thicknesses close or higher than the wavelength of the surface acoustic wave, the measured velocity of the Rayleigh surface mode mainly depends on the shear elastic constant through the simple relation $v_R = \beta(C_{44}/\rho)^{1/2}$, where β is a slightly dependent function of the other elastic constants.[8] The expected value of C_{44} for the superlattice was calculated from the C_{44} values of the two constituents, using the rule of the weighted harmonic average.[13] The retained C_{44} values for Mo(110) and Ni(111) polycrystalline layers are those corresponding to the so-called Hill average,[14] which is a median value between the Reuss and Voigt estimates.

Figure 2 displays the evolution with Λ of the shear elastic modulus determined by BLS. A huge elastic softening is observed with decreasing Λ, which gives evidence for the prime role of an *interfacial contribution*. It is worth pointing out that the drastic drop, which reaches -62% for $\Lambda = 20$ Å, is the strongest ever reported in the literature for metallic superlattices. In this context, it is interesting to notice that, under the present deposition conditions, the structure remains crystalline even for the smallest values of Λ, and no increase in C_{44} due to the formation of amorphous phases is observed for $10\,\text{Å} < \Lambda < 20\,\text{Å}$, as reported previously.[3–6] This suggests that the lattice collapse into an amorphous state could be a relaxation path for the system to avoid the mechanical instability.

A monotonous but very slight increase of $\bar{d}$ with decreasing Λ (not shown here: see Ref. 10) with no apparent correlation with the sharp elastic softening, is observed in the range 20–200 Å, in marked departure from previous studies of this system.[5,6] However, a clear correlation is found between the evolution of d_{Mo} (Fig. 3) and C_{44} with decreasing Λ. This significant and apparent reduction of d_{Mo} for $\Lambda < 250$ Å is quite striking since, intuitively, one would expect an augmentation due to the enhancement of the coherency stresses at small Λ owing to the epitaxial relationship between the two lattices.[15] Regarding d_{Ni}, its value is close to the bulk one, except for $\Lambda < 80$ Å where an increase is observed (Fig. 3). The anomalous behaviors of d_{Mo} and d_{Ni} for $\Lambda < 250$ Å, which cannot be explained in terms of elastic strains—if one takes into account the persistence of these variations after ion-induced stress relaxation[10,16]—suggest the presence of *alloyed layers*. This alloying effect, which

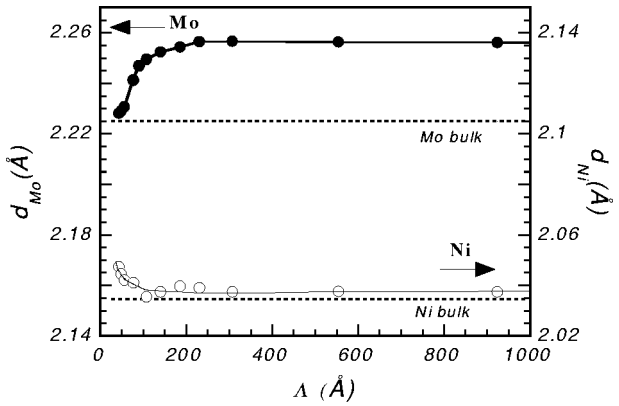

FIG. 3. Average Mo(110) and Ni(111) out-of-plane interplanar spacings determined by x-ray refinement vs Λ for the multilayers samples. The solid lines are drawn to guide the eyes.

had been mentioned earlier by Bain *et al.*,[17] but not correlated to the elastic behavior of the multilayers, is confirmed by recent investigations based on the determination of the stress-free lattice parameter.[10,15] Thus the apparent correlation observed between the variation of d_{Mo} and C_{44} with Λ seems to indicate that a chemical interfacial alloying could be responsible for the elastic softening.

In order to give a more quantitative proof of this statement, the experimental data of Fig. 2 were fitted using a model already proposed to account for interfacial effects.[6,9,13] Whereas interfacial atomic disorder or dilatation effects were previously introduced as cause for softening, the alloying effect is here explicitly taken into account. So we suppose that at every interface there is an alloyed layer of thickness t_{int} and, if isolated, would have a shear elastic constant C_{44}^{int}. The effective C_{44} elastic constant of the layered structure is then given by

$$\frac{\Lambda}{C_{44}} = \frac{t_{Mo}}{C_{44}^{Mo}} + \frac{t_{Ni}}{C_{44}^{Ni}} + \frac{2t_{int}}{C_{44}^{int}}, \tag{1}$$

where C_{44}^{Mo} (C_{44}^{Ni}) and t_{Mo} (t_{Ni}) are the shear elastic constant and effective thickness of the individual Mo (Ni) layers. By writing that $2t_{int}$ is the sum of two contributions δt_{Mo} and δt_{Ni}, which denote part of the nominal thickness t_{Mo}^{nom} and t_{Ni}^{nom} of the Mo and Ni layers involved in the formation of the alloyed interfacial layer, Eq. (1) becomes

$$\begin{aligned}\frac{1}{C_{44}} &= \left[\frac{t_{Mo}^{nom}/\Lambda}{C_{44}^{Mo}} + \frac{t_{Ni}^{nom}/\Lambda}{C_{44}^{Ni}}\right] \\ &\quad + \frac{2t_{int}}{\Lambda}\left[\frac{1}{C_{44}^{int}} - \left(\frac{\delta t_{Mo}/2t_{int}}{C_{44}^{Mo}} + \frac{\delta t_{Ni}/2t_{int}}{C_{44}^{Ni}}\right)\right] \\ &\equiv \left[\frac{1}{C_{44}^{\infty}}\right] + \frac{2t_{int}}{\Lambda}\left[\frac{1}{C_{44}^{int}} - \frac{1}{C_{44}^{eq}}\right],\end{aligned} \tag{2}$$

where C_{44}^{∞} is the effective value in the limit $\Lambda \to \infty$ (corresponding to an ideal superlattice) and C_{44}^{eq} traduces the effective value for an equivalent multilayer with a Mo/Ni thickness ratio equal to $\delta t_{Mo}/\delta t_{Ni}$.

The variation of $1/C_{44}$ as a function of $1/\Lambda$ is reported on Fig. 4. A linear dependence is observed for $\Lambda > 25$ Å in agreement with the proposed model [Eq. (2)], while for the smallest values of Λ, C_{44} remains constant, which allows one to obtain directly an estimate of the interfacial effective modulus: $C_{44}^{int} \sim 31$ GPa. The observed evolution is correctly reproduced when an interfacial alloy layer of thickness $t_{int} \sim 12$ Å is incorporated in the above model. This rather thick value of t_{int} means that chemical gradients extend to five to six atomic planes. During the deposition process, ballistic effects and/or an increased surface mobility due to the high energy of the incoming sputtered atoms may promote atomic exchanges on several atomic planes. Nevertheless, such a value of 12 Å is probably an overestimation of the real interfacial transition layer since it implicitly includes any contribution due to additional interfacial effects, such as atomic disorder.[9] The extrapolation at $1/\Lambda = 0$ gives $C_{44}^{\infty} = 64.5$ GPa. This latter value is lower (-20%) than the expected one for an ideal superlattice (80 GPa). This significant reduction suggests that volume effects also contribute to the elastic softening observed for the Mo/Ni superlattices. This could be attributed to the Mo sublayer since a reduction of C_{44} is observed for pure (110) Mo films (see legend of Fig. 5).

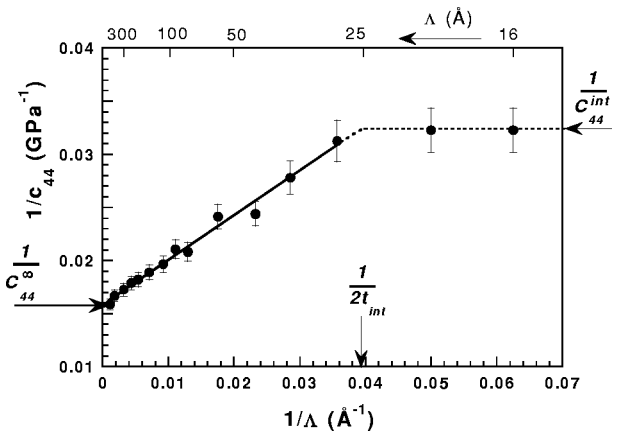

FIG. 4. Plot of $1/C_{44}$ vs $1/\Lambda$ (same data as in Fig. 2). Solid line is a fit to the experimental data using Eq. (2).

From the overall set of experimental data, the formation of an *interfacial alloyed layer* can be unambiguously put forward. Nevertheless, the direct link between such an alloying effect and the observed elastic softening remains to be demonstrated. For this purpose, BLS measurements were performed on $Ni_{1-x}Mo_x$ solid solutions obtained by cosputtering, in the entire composition range. Figure 5 reports the evolution of the C_{44} elastic constant versus the Mo atomic fraction. It can be seen that a drastic decrease in C_{44} (up to 40%–50%) occurs in the regions where crystalline solid solutions are formed. This clearly points out that the formation of metastable solid solutions in the Ni-Mo system induces an elastic lattice instability.

With increasing Mo or Ni atomic fraction, a dramatic structural transition into an amorphous phase occurs for $x_{Mo} \sim 0.28$ and $x_{Ni} \sim 0.27$. These values far exceed the equilibrium bulk solubility limits, which are, respectively, x_{Mo}

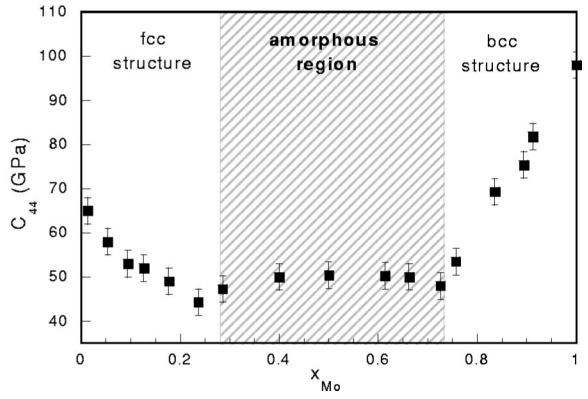

FIG. 5. C_{44} elastic constant (determined from BLS) vs Mo atomic fraction (x_{Mo}), for the $Ni_{1-x}Mo_x$ solid solutions. Note that for $x_{Mo} = 1$, the measured value of 98 GPa is below the expected one (127 GPa).

~ 0.13 and $x_{Ni} \sim 0$ at RT. It is here important to point out that the crystal to amorphous (c-a) transition is accompanied by a slight recovering of the shear elastic modulus. By contrast, as the solute concentration is further increased, C_{44} remains approximately constant and equal to 50 GPa. These results seem to indicate that the onset of the amorphization process is triggered by a mechanical instability: the c-a transition being a relaxation path to avoid the mechanical collapse (characterized by a vanishing shear modulus) of the metastable supersaturated crystalline solid solution. Random local shear stress fields due to the large difference in atomic size are assumed to be the root of the occurrence of a local atomic structural disorder, in good agreement with the argument originally proposed by Egami and Waseda.[18] This effect has been predicted by Zhang *et al.*[19] for Mo-rich solid solutions using molecular dynamics simulations. Such a close relation between the elastic softening and the structural disorder as precursors of the crystalline lattice collapse has been experimentally evidenced several times.[20–23]

The present results support the idea that the formation of a NiMo alloy at the interfaces is at the origin of the elastic softening observed in the Ni/Mo multilayers. Nevertheless, the extremely low value of $C_{44} \sim 31$ GPa observed for $\Lambda < 20$ Å is never reached for $Ni_{1-x}Mo_x$ alloys produced by cosputtering deposition, neither at the crystalline state nor at the glassy state. This suggests that a *supersaturated crystalline* alloyed interfacial layer could be stabilized within the composition range where amorphous phases are formed (see Fig. 5). In multilayered systems, such a stabilization of nonequilibrium phases under epitaxial growth, by reducing the surface and/or elastic strain energies, can be favored.[24] Several mechanisms involving atomic exchanges on only a few atomic planes may promote an intermixing: dynamical surface segregation, stress-induced chemical alloying, or ballistic effects. Further studies on the influence of the growth conditions (energy and flux of the sputtered atoms, temperature, etc.) should give insights into the understanding of the intermixing effect.

In summary, the present study provides convincing evidence that the huge elastic softening observed in Ni/Mo multilayers, which reaches -62% for $\Lambda \sim 20$ Å, is correlated with the stabilization of a metastable interfacial alloyed layer into a crystalline state. The drastic drop in the shear elastic modulus of crystalline $Ni_{1-x}Mo_x$ solid solutions, when the induced solubility is increased, supports this interpretation. Additional experiments based on the diffraction anomalous fine-structure technique should give insights into the local chemical environment of the interfaces. The present results also provide enlightenment on the frequently reported anomalous elastic properties of metallic multilayers.

*Corresponding author. Electronic address: gregory.abadias@univ-poitiers.fr

[1] For a review, see, e.g., I. K. Schuller, A. Fartash, and M. Grimsditch, MRS Bull. **15** (10), 33 (1990) and references therein.
[2] W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **48**, 876 (1977).
[3] A. Kueny, M. Grimsditch, K. Miyano, I. Banerjee, C. M. Falco, and I. K. Schuller, Phys. Rev. Lett. **48**, 166 (1982).
[4] E. E. Fullerton, S. Kumar, M. Grimsditch, D. M. Kelly, and I. K. Schuller, Phys. Rev. B **48**, 2560 (1993).
[5] M. R. Khan, C. S. L. Chung, G. P. Felcher, M. Grimsditch, A. Kueny, C. M. Falco, and I. K. Schuller, Phys. Rev. B **27**, 7186 (1983).
[6] B. M. Clemens and G. L. Eesley, Phys. Rev. Lett. **61**, 2356 (1988).
[7] I. K. Schuller and A. Rahman, Phys. Rev. Lett. **50**, 1377 (1983).
[8] G. Carlotti, D. Fioretto, G. Socino, B. Rodmacq, and V. Pelosin, J. Appl. Phys. **71**, 4897 (1992).
[9] D. Wolf and J. F. Lutsko, J. Appl. Phys. **66**, 1961 (1989).
[10] J. Pacaud, F. Martin, A. Michel, C. Jaouen, Ph. Djemia, and F. Ganot, in *Polycrystalline Metal and Magnetic Thin Films—2000*, edited by L. Gignac, O. Thomas, J. MacLaren, and B. Clemens, Mater. Res. Soc. Symp. Proc. No. 615 (Materials Research Society, Pittsburgh, 2001), pp. G8.7. 1-6.
[11] E. E. Fullerton, I. K. Schuller, H. Vanderstraeten, and Y. Bruyneseraede, Phys. Rev. B **45**, 9292 (1992).
[12] R. Loudon, Phys. Rev. Lett. **40**, 581 (1978).
[13] M. Grimsditch and F. Nizzoli, Phys. Rev. B **33**, 5891 (1986).
[14] R. Hill, Proc. Phys. Soc., London, Sect. A **65**, 349 (1952).
[15] F. Martin, J. Pacaud, G. Abadias, C. Jaouen, and Ph. Guerin, Appl. Surf. Sci. **188**, 90 (2002).
[16] J. Pacaud, G. Abadias, F. Martin, and C. Jaouen, (unpublished).
[17] J. A. Bain, L. J. Chyung, S. Brennan, and B. M. Clemens, Phys. Rev. B **44**, 1184 (1991).
[18] T. Egami and Y. Waseda, J. Non-Cryst. Solids **64**, 113 (1984).
[19] Q. Zhang, Z. C. Li, B. X. Liu, and E. Ma, J. Appl. Phys. **87**, 4147 (2000).
[20] L. E. Rehn, P. R. Okamoto, J. Pearson, R. Bhadra, and M. Grimsditch, Phys. Rev. Lett. **59**, 2987 (1987).
[21] C. E. Krill III, J. Li, C. M. Garland, C. Ettl, K. Samwer, W. B. Yelon, and W. L. Johnson, J. Mater. Res. **10**, 280 (1995).
[22] J. Chevrier, J. B. Suck, J. C. Lasjaunias, M. Perroux, and J. J. Capponi, Phys. Rev. B **49**, 961 (1994).
[23] A. Siedel, S. Massing, B. Strehlau, and G. Linker, Phys. Rev. B **38**, 2273 (1988).
[24] G. Abadias, I. Schuster, A. Marty, and B. Gilles, Phys. Rev. B **61**, 6495 (2000).