Ultrasonic and atomic force studies of the martensitic transformation induced by temperature and uniaxial stress in NiAl alloys

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The single-crystal elastic constants were measured in NiAl alloys with nickel compositions between 49.4 and 63 at. %. For Ni compositions in excess of 61 at. %, the crystals undergo a martensitic transformation. The transformation was studied as a function of temperature and uniaxial stress using ultrasonic, optical, and atomic force microscopy techniques. Uniaxial stress applied along the [001] direction on $Ni_{63}Al_{37}$ crystals induced a transformation and yielded a value of $dM_S/d\sigma = 0.53$ K/MPa. Atomic force microscopy measurements yield quantitative information of the surface relief associated with the transformation and provide clear evidence of a surface transformation occurring approximately 5 K prior to the bulk transformation as determined by ultrasonic measurements. The results are compared with earlier studies of the elastic constants and with neutron-diffraction studies of the temperature and stress dependence of the slow transverse-acoustic branch in NiAl. [S0163-1829(99)00205-2]

INTRODUCTION

The martensitic phase transformation in Ni_xAl_{1-x} alloys has been extensively studied in recent years in an attempt to obtain a fundamental understanding of the transformation in this shape memory alloy system. NiAl alloys undergo a martensitic transformation from a CsCl structure type to a $7R$ structure below the transformation temperature for Ni compositions in excess of 61 at. %. The transformation temperature, M_S, in these shape memory alloys increases by approximately 140 K per at. % Ni. Many of the studies focused on the precursor effects which are present in this system. These studies included optical microscopy, elastic and inelastic neutron diffraction, x-ray diffraction, thermal-expansion measurements, high-resolution transmission electron microscopy, and ultrasound.[1–11] In many of these studies, precursor effects were observed at temperatures well above the bulk phase transition temperature.

The neutron-scattering experiments have clearly established the existence of a soft phonon mode in the slow transverse-acoustic (TA_2) branch.[2] As evidence of the softening, a dip in the phonon-dispersion curve was seen well above the actual transformation temperature. In $Ni_{62}Al_{38}$ ($M_S = 80$ K) the anomaly in this phonon branch occurs at $\zeta = 0.14$, well above M_S, and becomes more pronounced as M_S is approached. At the same wave vector an elastic diffuse central peak is also found, and its intensity increases as M_S is approached. The uniaxial-stress dependence of the phonon behavior in the premartensitic phase of this system has also been studied.[4] Uniaxial stress has an effect similar to that of temperature on the behavior of the soft mode in the TA_2 branch. The dip in the phonon-dispersion curve is stress dependent and shifts from $\zeta = 0.14$ at zero stress to $\zeta = 0.18$ for an applied uniaxial stress of 85 MPa applied in the [0 0 1] direction at room temperature. As the temperature is lowered, the dip shifts to higher values of ζ and becomes more pronounced. These neutron studies, along with x-ray-diffraction studies, also show that M_S increases with uniaxial stress.[5] It is interesting to note that a later study performed on a nontransforming $Ni_{60}Al_{40}$ crystal showed a similar precursor behavior in the stress dependence of phonons and the associated elastic diffuse scattering, although the crystal did not transform for stress as high as 168 MPa applied for temperatures as low as 10 K.[4]

Linear thermal-expansion measurements on a $Ni_{62.5}Al_{37.5}$ single crystal showed a pretransformation effect as high as 115 K above M_S.[6] This effect coincided with optical observation of surface relief. High-resolution transmission electron microscopy (HRTEM) studies at room temperature provided direct evidence of the premartensitic microstructures in $Ni_{63}Al_{37}$ single crystals.[7] These samples exhibited an assembly of nonuniformly dispersed and micromodulated domains which is consistent with $[1\,1\,0]\,\langle 1\bar{1}0\rangle$ shear plus shuffle displacements. This is the shear strain associated with the slow transverse-acoustic branch at $q = 0$ discussed above. The HRTEM studies also showed the stress-induced transformation by focusing on a sharp tip of a microcrack in their NiAl foil produced during the electropolishing process and clearly shows the progression of the transformation from regions of low stress to regions of high stress. Far away from the crack, the structure is characteristic of the high-temperature phase. These studies have led to models which suggest that highly localized strain centers are the transformation embryo from which the product-phase nuclei are formed. Clapp has combined the soft-mode concept and the presence of defects in the sample by developing a localized soft-mode model for nucleation.[12] The model suggests that around a particular defect a combination of stresses and strains can cause a mode to soften near the defect and thereby serve as a center for nucleation. The behavior of elastic constants as a function of uniaxial stress and temperature, and the use of atomic force microscopy (AFM) as a potential elastic probe can provide valuable information regarding the nature of this transformation.[13] Studies of this behavior using an AFM can also provide a stringent test of various theoretical models developed to explain the premartensitic effects in the transformation in this system.

The single-crystal elastic constants and their temperature derivatives were determined for alloys with compositions between 49.4 and 63 at. %. In addition, three experimental methods were employed to study the structural phase transformation in two $Ni_{63}Al_{37}$ alloys. The first of these was an optical micrograph study of the martensite bands which form on the (1 1 0) and (0 0 1) surfaces as the temperature is lowered through M_S. Optical micrographs of the martensite bands that form on (1 1 0) faces as uniaxial stress is applied in the [0 0 1] direction were also obtained. The second method was an ultrasonic study of the elastic properties of the samples as a function of temperature and as a function of uniaxial stress applied along either the $[1\bar{1}0]$ or the [0 0 1] directions. These measurements were used to determine the bulk transition temperature and the stress dependence of the transition temperature. The third method employed an atomic force microscope to study the surface relief as a function of temperature and uniaxial stress.

All of these experiments were done on each of the $Ni_{63}Al_{37}$ samples so that a direct correlation between the bulk transformation and surface relief could be made. The atomic force measurement can provide unique, valuable, three-dimensional (3D) information about the surface relief as the sample is stressed or cooled. In addition, the AFM probe has the potential to measure the variation in local elastic properties and thereby to provide valuable information about the nucleation process.[13]

EXPERIMENTAL

The single crystals used in the present study had Ni compositions between 49.4 and 63 at. %. The crystals were oriented with faces perpendicular to the [1 1 0] direction to determine the three independent elastic constants. In addition, two sets of faces oriented perpendicular to the $[1\bar{1}0]$ and [0 0 1] directions were prepared so that variation of the martensitic transformation temperature with stress could be studied. The final polishing of the faces was done with a 0.05 μm powder.

The absolute elastic constants were determined using an ultrasonic pulse echo technique and a magnesium buffer rod. The buffer rod eliminates the transit error associated with mounting the transducer directly on the sample.

The temperature dependence and stress dependence of the elastic constants were determined by mounting the transducer directly on the sample and measuring the change in transit time either by a pulse overlap method or direct measurement of the change in transit time with a LeCroy oscilloscope.

The stress dependence of the martensitic transformation temperature was studied for two $Ni_{63}Al_{37}$ single crystals (martensitic transformation temperature of approximately 285 K). The study included ultrasonic and atomic force microscopy techniques. A Park Scientific Instruments Autoprobe Stand-Alone® atomic force microscope was employed to study the thermally and stress-induced surface relief which accompanies the transformation. In this instrument, the piezoresistive tip scans the sample so that measurements as a function of stress and temperature can be readily made.

TABLE I. The density, length, absolute velocity associated with the three independent elastic constants along with martensitic phase transformation temperature M_S for Ni_xAl_{1-x} alloy single crystals at 22 °C.

Sample (at. % Ni)	Density (g/cm^3)	Length (cm)	V_L	V_{44} (10^5 cm/s)	V'	M_S (K)
49.4	5.964	9.95	6.944	4.400	2.410	
50.0	5.994	9.62	6.918	4.412	2.403	
62.0	6.590	6.50	6.555	4.244	0.899	95
62.5	6.644	9.7	6.533	4.25	0.821	180
63.0	6.657	9.625	6.534	4.253	0.729	280

RESULTS AND DISCUSSION

A. Elastic constants

Table I shows the results of the absolute velocity measurements associated with the three independent elastic constants $C_L=(C_{11}+C_{12}+2C_{44})/2$, C_{44} and $C'=(C_{11}-C_{12})/2$. The measured transformation temperature and the density are also shown. The velocity associated with C' is seen to decrease rapidly as the Ni composition is increased.

The room-temperature elastic constants obtained from these velocity measurements are shown in Table II. Also shown for comparison purposes are the results of Rusovic and Warlimount and Enami *et al.*[8,10] The most striking features in the data are the large decrease in C' and the large increase in elastic anisotropy, $A=C_{44}/C'$, as the Ni composition is increased. The extremely high elastic anisotropy is typical of β-phase alloys which undergo structural transformations. Among the elements, the largest elastic anisotropy is present in the alkali metals. For example, lithium, which undergoes a martensitic phase transformation, has an elastic anisotropy of 9 at 77 K.

For the 49.4 at. % crystal all three elastic constants stiffen as the temperature is lowered. However, the temperature derivative for the C' mode becomes positive for Ni concentra-

TABLE II. The single-crystal elastic constants and elastic anisotropy, $A=C_{44}/C'$, of Ni-Al alloys at 22 °C.

Sample (at. % Ni)	C_L	C_{44}	C' (10^{12} dyn/cm^2)	C_{11}	C_{12}	λ
49.4	2.876	1.155	0.346	2.067	1.375	3.4
50.0	2.868	1.168	0.346	2.046	1.354	3.4
62.0	2.832	1.187	0.0521	1.697	1.593	22.8
62.5	2.836	1.200	0.0448	1.681	1.591	26.8
63.0	2.842	1.204	0.0354	1.673	1.612	34.0
50.0[a]	2.828	1.131	0.356	2.053	1.341	3.2
55.0[a]	2.890	1.199	0.210	1.901	1.481	5.7
60.0[a]	2.862	1.205	0.086	1.743	1.571	14.0
62.0[a,b]	2.863	1.205	0.044	1.702	1.654	27.4
62.5[a,b]	2.867	1.206	0.034	1.695	1.627	35.5
63.0[a,b]	2.873	1.207	0.025	1.691	1.641	48.3
63.2[c]	2.822	1.306	0.151	1.667	1.356	8.7

[a]Reference 8.
[b]Reference 9.
[c]Reference 10.

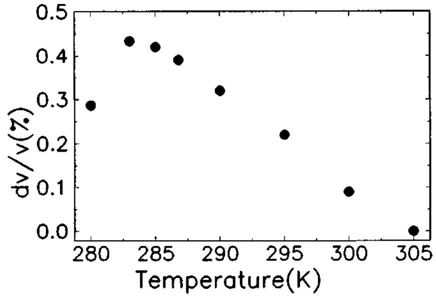

FIG. 1. Temperature dependence of the velocity associated with the elastic constant C_{44}, a crystal with a Ni composition of 63 at. %.

tions in excess of 61 at. %. In contrast, the elastic constants C_L and C_{44} and their temperature coefficients are not strongly dependent on the amount of Ni present. While no other direct measurements of the elastic constants exist for Ni compositions between 62 and 63 at. %, extrapolated results are very similar to those obtained in the present study.[9] The data of Enami *et al.* obtained on a 63.2 at. % crystal are comparable to the present results on $Ni_{63}Al_{37}$, for C_L and C_{44} but differ significantly for the elastic constant C'. The elastic constant C' was not directly measured in their study but computed from measured values of C_L, C_{11}, and C_{44} and therefore is not as accurate as the present directly measured value C'. The adiabatic bulk modulus and Young's modulus can also be computed from the measured elastic constants for each of the alloys. The bulk modulus determined from our measurements has a value of 1.61×10^{12} dyn/cm^2 and is essentially independent of Ni composition. Young's modulus, however, decreases from 0.97 to 0.09×10^{12} dyn/cm^2 as the Ni composition is increased from 49.4 to 63 at. %. For cubic materials, Young's modulus is determined primarily by the elastic constant C', so this dependence of Young's modulus on composition is expected.

The ultrasonic attenuation and velocity in the vicinity of the martensitic transformation temperature were also studied as a function of temperature and uniaxial stress for waves associated with the three independent elastic constants C_L, C_{44}, and C' for a crystal with an Ni composition of 63 at. %. The temperature dependence of the velocity associated with the fast transverse branch at $q=0$ and with the elastic constant C_{44} is shown in Fig. 1. The velocity initially increases as the temperature is lowered, but a decrease in the velocity does occur near but above the transition temperature. The temperature dependence of the ultrasonic attenuation and velocity associated with the elastic constant C_L is shown in Fig. 2(a) for a $Ni_{63}Al_{37}$ crystal. The velocity associated with this mode exhibits behavior similar to that of the fast shear velocity prior to the transformation. Arbitrarily, the attenuation at the point where one half the change occurred was chosen as the bulk transformation temperature, M_S, which is approximately 285 K. Figure 2(b) shows the temperature dependence of attenuation and velocity associated with the elastic constant C'. Note that the velocity for the C' mode first decreases linearly and then decreases more dramatically prior to the transformation. This softening is often considered to be a precursor of the transformation and the signature of an incipient lattice stability. The temperature

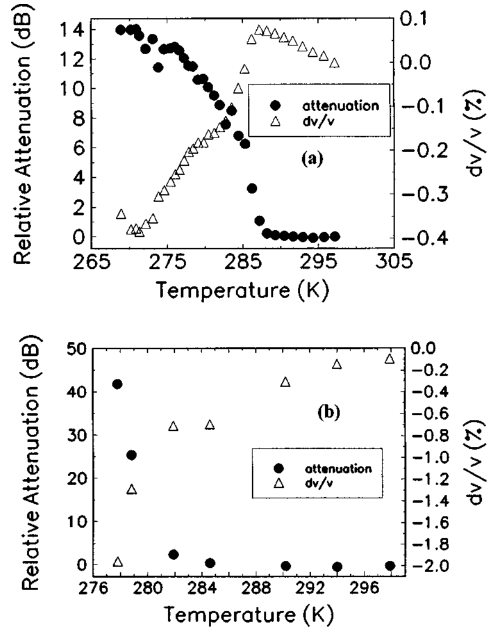

FIG. 2. (a) The relative attenuation and percentage fractional velocity with elastic constant C_L as a function of temperature. (b) Corresponding results for C', a crystal with a Ni composition of 63 at. %.

dependence of the velocity associated with the slow transverse mode is consistent with the inelastic neutron scattering results for the TA_2. One should note that, for the longitudinal mode, a decrease in the velocity also occurs near the onset of the transformation which is concurrent with the increase in the ultrasonic attenuation.

The uniaxial stress dependence for the two modes shown in Figs. 3(a) and 3(b) are for the elastic constants C_L and C',

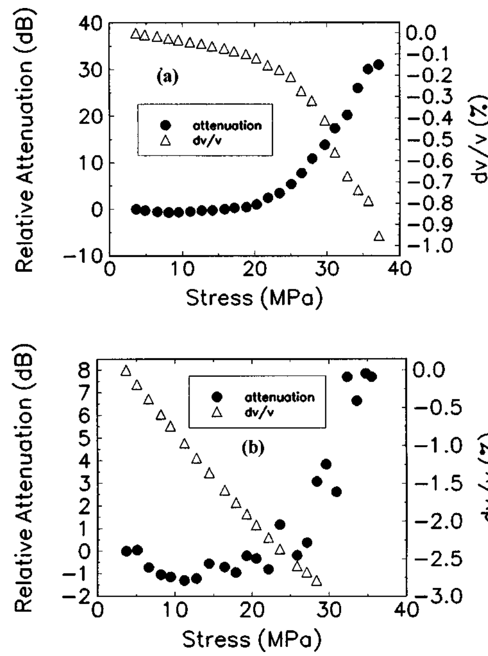

FIG. 3. (a) The relative attenuation and percentage fractional velocity associated with the elastic constant C_L for uniaxial stress along a [001] direction at 297 K. (b) Corresponding results for C', a crystal with a Ni composition of 63 at. %.

respectively. The stress was applied along the [001] axis at $T=297$ K in both cases. Using the same arbitrary definition for M_S which was used in the thermally induced transformation study, as stated above, we found that the transition occurs at approximately 30 MPa for both the longitudinal and slow transverse modes. This gives a value of $dM_S/d\sigma=0.43$ K/MPa for the longitudinal mode and $dM_S/d\sigma=0.63$ K/MPa for the slow transverse mode. The average value of 0.53 compares favorably with the value of 0.63 taken from x-ray data on a crystal of the same nominal composition. The [001] uniaxial stress dependence was also studied at 289 K. As expected, less stress is needed to induce the transition at this temperature. Figure 3(b) clearly shows that the velocity associated with C' decreases rapidly with increasing stress in the vicinity of M_S which change is very similar to the temperature dependence of C' in the vicinity of M_S. The stress dependence of C', together with the neutron-scattering studies of the uniaxial-stress dependence of the phonon behavior for the slow transverse acoustic branch, show that this entire branch softens with increasing stress applied along the [001] direction. This softening of the elastic constant C' with applied uniaxial stress lends support to the localized soft-mode theory for nucleation.[3,12] The velocity data shown in Figs. 3(a) and 3(b) have not been corrected for length changes associated with the Poisson effect, but this correction is of the order of a few tenths of a percent for a stress of 300 MPa.

Ultrasonic measurements with uniaxial stress along the $[1\bar{1}0]$ direction were also made. No surface relief bands appear on any of the other four faces when the sample is stressed in this direction, and no evidence of bulk attenuation is observed for stresses up to 50 MPa, the highest applied stress used in this study.

The values of $dM_S/d\sigma$ obtained in the present study varied between 0.40 and 0.50 K/MPa. The average value of 0.45 K/MPa, obtained by ultrasonic measurement, is smaller than the value of 1.4 K/MPa obtained in the neutron study on a $Ni_{62.5}Al_{36.5}$ alloy, but comparable to the value of 0.63 K/MPa obtained in the x-ray study on a $Ni_{63}Al_{37}$ alloy.[3,5] The difference in these values may be due to the presence of shear components in the applied stress direction and to the fact that $dM_S/d\sigma$ is most likely dependent upon Ni composition. All of the studies, however, show that uniaxial stress applied along a [001] direction increases M_S in a dramatic way. Our studies of the pressure derivatives of the elastic constants in NiAl alloys showed that M_S decreases with increasing hydrostatic pressure, and all the pressure derivatives of the elastic constants are positive.[14]

B. Optical and atomic force microscopy

Martensitic bands associated with surface relief are readily observed on all faces of the $Ni_{63}Al_{37}$ samples when cooled. The onset of surface relief was approximately 287 K for a properly annealed sample on a polished (110) face. (The formation of bands occurred at slightly lower temperatures on a surface that was not polished or annealed in this manner.) The second sample studied showed surface relief at 291 K.

Optical micrographs were also used in the study of surface relief induced by uniaxial stress. The stress needed to induce surface relief was a strong function of temperature, surface preparation, and a placement of the sample in the stress apparatus. At 297 K, a 0.05 μm-polished (110) face showed surface relief at 29 MPa, while an electropolished (110) face showed surface relief at 24 MPa. In addition, as expected the bands generally appeared at a lower stress for a lower temperature. Typical values of $dM_S/d\sigma=0.4$ to 0.5 K/MPa from the optical data are in agreement with the results obtained from the ultrasonic studies done on the same crystals. While the same thermally induced bands generally appeared in various reproducible domains on the surface, stress-induced bands often appeared at 45 degree angles to the stress direction. The pattern, however, could change from run to run, most likely due to changing shear stress components intrinsic to the placement of the sample within the stress apparatus, although copper spacers were employed to reduce the shear components in our apparatus.

Further insight into the nature of the surface bands and precursor effects was obtained using an atomic force microscope. The only other study of this type was a quantitative study of surface relief in Cu-Al-Ni shape memory alloys using scanning tunneling microscopy in which the height of the surface bands and the surface relief angle of the different variants were determined.[15] The focus of the present AFM study was to determine the temperature and stress dependence of the martensitic bands. Two studies are included in this section: one is a study of the growth of a surface relief ''spear'' as a function of decreasing temperature, and the other is a study of the growth of stress bands as a function of increasing [001] uniaxial stress.

Thermally induced bands could be observed from a height of 20 nm to a height of 3 μm when the band is fully developed. An AFM image of one of the spear bands at $T=285$ K in a given domain is shown in Fig. 4(a). A 3D image of the same band at the same temperature is shown in Fig. 4(b). It should be noted that this type of band has an isosceles-triangle-like cross section. The diagonal line shown in Fig. 3 is a polishing scratch and was used as a reference. The most rapid growth of a particular spear band occurs over approximately 1 K change in temperature, The thermally induced band at $T=284$ K is shown in Fig. 5. Note that both the height and width of the band increase an order of magnitude for a 1 K change in temperature. The temperature-induced surface relief study in the Cu-Al-Ni shape memory alloy by scanning tunneling microscope was done near room temperature ($M_S=296$ K).[15] The height of the surface relief is several hundred nanometers. These heights are comparable to those shown in Fig. 4 for $Ni_{63}Al_{37}$. Our study, however, shows that when the bands become fully developed that the height as well as the width increase by an order of magnitude while the surface relief angles remain essentially constant.

A second sample of the same nominal composition was also studied. The AFM studies on this sample have shown that, for an area near a defect, the formation of bands at 297 K can be detected. The height of the surface relief band at this temperature was only 17 nm, which is comparable to the surface roughness in the region scanned. The corresponding width of the band was 1.9 μm. The formation of the band was developed slowly and easily followed as the temperature was decreased. At 290 K the band had a height of only 30 nm. The band then grew rapidly, and at 289 K had a height

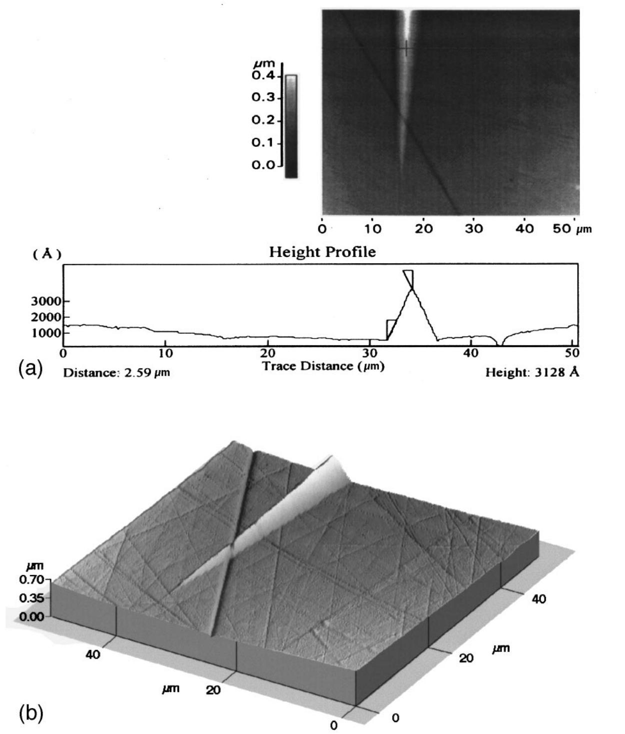

FIG. 4. (a) An AFM image at 285 K of a thermally induced martensitic band. The chart represents the X-Z cross section indicated by the horizontal line in the upper image. The cursors in the chart correspond to the vertical marks in the upper image. (b) Same image in three dimensions.

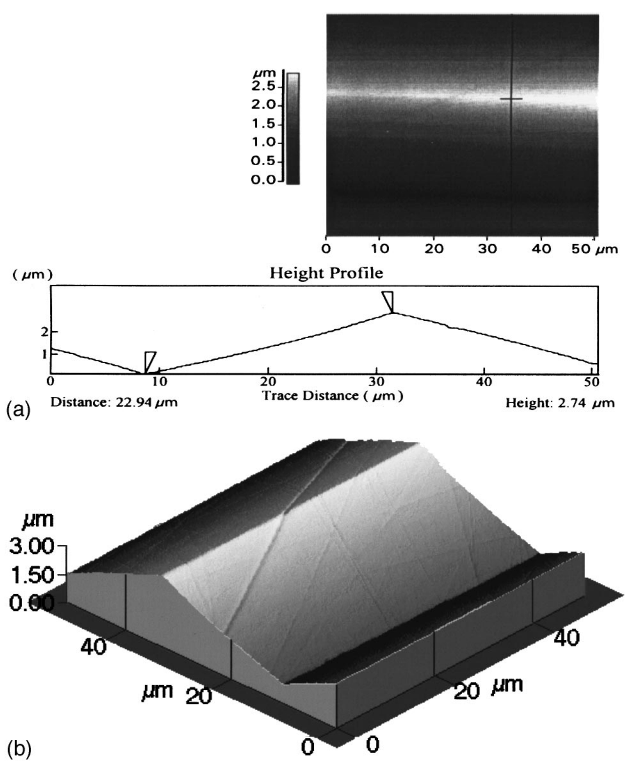

FIG. 5. (a) An AFM image of the same band shown in Fig. 4 at $T = 284$ K. (b) The same image in three dimensions.

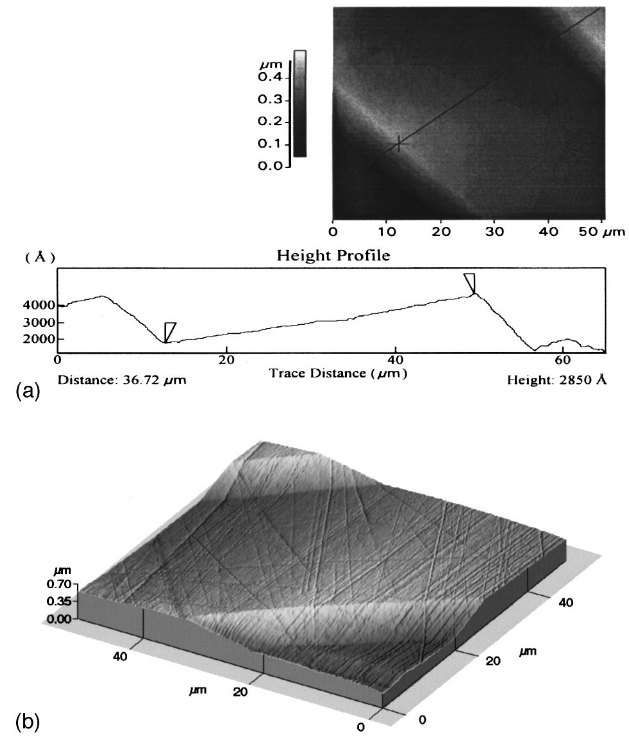

FIG. 6. An AFM image of a stress-induced band.

of 272 nm and a width of 19 μm. The region where the band developed was very close to a region of high internal stress. This latter region contained small surface relief bands even above room temperature. These bands, however, did not vary with temperature and were overcome by the thermally induced band at 289 K. It is clear from these studies that surface preparation and surface defects can lead to a variety of results. However, even in this sample the band can be detected by AFM 6 K above where it can be observed optically, and the fully developed optical bands occurred very close to the onset of the bulk transition for both samples. Since it has been clearly established that M_S increases with stress, it is not surprising that a region on a surface with a local defect, and therefore with a high internal stress transforms near room temperature.

The uniaxial stress study performed on the same (110) face (first sample) showed a different kind of band formation. An AFM image is shown in Fig. 6. The *XZ* chart shows that the cross section for this band is not an isosceles triangle. When the stress band is fully developed, the height is 0.3 μm which measurement is an order of magnitude smaller than that of the thermally induced bands. It is possible that large stresses could increase the size of the bands. We, however, chose to limit the applied stress to avoid damaging the sample.

SUMMARY

The behavior of the temperature and stress dependence of the velocity associated with the TA_2 branch is consistent with the neutron data. The present experiments on 63 at. % NiAl alloys using both a surface probe (AFM) and a bulk probe (ultrasound) showed that both thermally induced and stress-induced transformations emanate on the surfaces and spread to the bulk at lower temperature or higher stress. The temperature needed to induce the bulk transformation in these samples is only a few degrees lower than that needed to induce the surface transformation. These results are much different from the results of thermal-expansion measurements on a 62.5% alloy where precursor effects were observed nearly 100 K above the transformation temperature.[6] The ultrasonic measurements done both as a function of temperature and stress yield a value of $dM_S/d\sigma = 0.53$ K/MPa on a 63.0 at. %, which is comparable to the value obtained from x-ray data. While the direct observation of the tweed with an AFM is difficult because of problems associated with surface roughness and surface oxides, surface relief bands were observed with heights as small as 17 nm and these bands appear at temperatures slightly higher than when they are observed optically. The present AFM measurements are consistent with HRTEM done on foils and support theoretical models that assume that highly localized stress centers are the transformation embryo from which the transformation proceeds. The present measurements indicate that such embryos are most likely to occur at the surface and proceed into the bulk as either the temperature is lowered or the stress is increased. The present AFM and ultrasonic studies are consistent with the neutron and HRTEM studies. These measurements show that C' decreases with increasing stress and provide additional support of the localized soft-mode (LSM) theory.[12] Studies of the third-order elastic constants are in progress and will provide valuable information regarding the conditions for lattice stability and the critical shear stress in this alloy system and provide a more quantitative test for the LSM theory.

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