Mixture of Ordered Domains in the NiAl(111) Surface

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The atomic structure of the NiAl(111) surface has been investigated through a LEED *I-V* analysis. In order to achieve a unique, consistent agreement between experimental and calculated *I-V* spectra, this surface is determined to be a 50%-50% mixture of two ordered domains, one of which is Al terminated and the other is Ni terminated. The relaxations of the outermost interlayer spacings in each domain have been determined as well, and they are different for the two domains. The NiAl(111) surface is the first reported example of a binary-alloy surface in which a mixture of ordered domains with differing terminations coexists.

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The atomic structure of the NiAl(111) surface has been investigated by an analysis of low-energy electron diffraction (LEED) current versus energy (*I-V*) spectra. Initially an interesting dilemma was encountered in the analysis, since two quite different structural models for the surface, one for a Ni termination and one for an Al termination, lead to comparable agreement between calculated and experimental spectra. However, much better agreement was eventually obtained and the dilemma resolved by the consideration of the NiAl(111) surface to be a mixture of Ni-terminated and Al-terminated domains. Evidence is presented to demonstrate that the surface is a mixture of equal numbers of the two domains, subsequently referred to as a 50%-50% mixture. This is the first time that domains of different structure have been reported to coexist in the surface of a single crystal of a binary alloy. In addition, the results of the analysis indicate another novel feature exists in the surface, since the interlayer relaxations within the Ni-terminated and Al-terminated domains are significantly different.

Only a limited number of studies have been reported in which detailed information has been obtained about the surface atomic structure of ordered intermetallic compounds. Noteworthy studies have been done for Cu_3Au(100),[1] NiAl(110),[2] and the (100), (110), and (111) surfaces of Ni_3Al,[3-5] all of which can be prepared such that (1×1) diffraction patterns can be obtained. The atomic structure identified for each of these surfaces has a simple relationship to the stacking sequences of the respective crystal's bulk atomic layers. For example, all bulk (110) layers of NiAl have an equal number of Ni and Al atoms, while all bulk (111) layers of the Ni_3Al are composed of a 3-to-1 ratio of the Ni to Al atoms. The outermost layers of both NiAl(110) and Ni_3Al(111) have been determined[2,4] to have the same atomic composition as that of the respective bulk layers. However, the outer layers are relaxed from truncated bulk positions and they have a rippled reconstruction. Cu_3Au and Ni_3Al have the $L1_2$ crystal structure; therefore the bulk (100) layers alternate such that one layer is either all Cu or Ni and the next layer is an ordered lattice of either a composite of Cu and Au or Ni and Al. It has been reported[1,3] for both cases that the outermost (100) layer is the composite layer. Although the unit cell is rectangular instead of square, the stacking sequence of bulk (110) Ni_3Al layers is similar to the (100) stacking. Ni_3Al(110) also has been reported[5] to terminate with a composite layer of Ni and Al atoms.

Since NiAl has the CsCl structure, its bulk (111) layers consist of alternating layers of ordered lattices with either all Al atoms or all Ni atoms which are separated by a small interlayer spacing of 0.83 Å. If NiAl could be cleaved along a (111) plane, a given surface would then be terminated by either a Ni layer of an Al layer. However, (111) is not a cleavage plane and the NiAl(111) surface must be prepared by cleaning and annealing processes, which can introduce defects, such as steps, at the surface. Therefore, at least three terminations are possible for NiAl(111)-(1×1): It could be terminated only by Ni layers, only by Al layers, or by some mixture of these two. The termination which exists depends on the specific surface energies of the Ni and Al layers, on step wall energies, and possibly the details of the preparation processes.

A principal concern when starting to work on the NiAl(111) surface was whether a well-characterized surface could be prepared repeatedly. We found that a clean, well-ordered, reproducible surface could be prepared by mechanically polishing a crystal, aligned to be parallel to a (111) plane, and then cleaning it with cycles of Ar-ion sputtering and annealing at 875 °C.[6] After such preparation the surface-region Ni-to-Al ratio was approximately 1:1 as measured by Auger peak intensities with use of a cylindrical mirror analyzer, and the surface was clean to within the detection limits of the cylindrical mirror analyzer. Also, a sharp (1×1) LEED pattern was observed.

In addition to our identifying a prescription to prepare a well-ordered, stoichiometric, (1×1) surface, experiments were made to assess whether the preparations could influence the surface composition and order. Since the (111) planes are not NiAl cleavage planes, the preparation of a clean surface required low-energy Ar^+-ion sputtering and annealing, which alters the surface crystallinity and stoichiometry. In addition to removing surface contamination, Ar^+-ion sputtering preferentially depletes the Al concentration at the surface. However, at temperatures as low as 400 °C, Al begins to resegregate to the surface, and the surface damage is partially repaired. By 600 °C the Al-to-Ni ratio reaches a 1:1 equilibrium level, as determined by comparison of the measured Auger peak heights for the *MVV* (61 eV) and *LVV* (848 eV) Ni Auger transitions and the *LVV* (68 eV) and *KVV* (1396 eV) Al transitions to a calibration standard. In addition, the surface is well ordered as demonstrated by a well-focused LEED pattern and low background. However, a trace of C remains at the surface ($<1\%$ of a monolayer). The only detectable change at the surface following anneals between 600 and 900 °C is the removal of the C impurity. Finally between 900 and 1000 °C, a weak $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern could be observed. Since the NiAl alloy may have an irreversible order-disorder phase transition in the bulk between 1000 and 1300 °C, the sample was never annealed to temperatures above 1000 °C. The surface did not exhibit thermal surface roughening, which would be detectable by changes in the LEED pattern, nor any condition which depended on the history of the surface treatment, only on the sputtering and temperature cycling.

With the crystal aligned normal to the electron beam (typically to better than 0.1°), LEED *I-V* spectra were measured with techniques which have been used in previous analyses of surfaces.[7] Spectra were obtained for all LEED beams in a symmetrically equivalent set, and these were then averaged to obtain a spectrum used in the subsequent analysis.[8] For NiAl(111), *I-V* spectra were measured for seven sets of inequivalent LEED beams over the energy range of 50 to 300 eV.

To obtain information about the atomic structure of NiAl(111), the experimental *I-V* spectra were compared with spectra resulting from dynamical LEED calculations. Since perturbative techniques were judged to be unreliable due to the small interlayer spacing, the giant matrix inversion technique defined by Eq. (4.49) of Pendry[9] was employed. A sixteen-layer slab was used, and the calculations utilized full symmetrization. Results given here are based on calculations using a value of 4.5 eV for the imaginary component of the optical potential and Debye temperatures of 350 and 500 K, respectively, for the Ni and Al atomic sites. Eight phase shifts were employed, which were obtained from band-structural potentials furnished by Moruzzi.[10] Calculations were performed for over 160 (220) models for the Ni-terminated (Al-terminated) surface, in which the relative changes from bulk of the first, Δd_{12}, and second, Δd_{23}, interlayer spacings were varied. The calculated *I-V* spectra were compared with the experimental spectra visually, and by use of the Zanazzi-Jona[11] (R_{ZJ}) and the mean-square-difference[12] (R_2) reliability factors.

Initially we limited the analysis by assuming that the NiAl(111) surface would be terminated by either a layer of all Al atoms or by a layer of all Ni atoms. As illustrated by Fig. 1, such an assumption leads to a dilemma. Calculated *I-V* spectra for each of the two pure terminations were obtained for variations of Δd_{12} and Δd_{23}, which produced approximately equal agreement with the experimental *I-V* spectra. Also, each analysis of the terminations leads to a seven-beam total R_{ZJ} of about 0.09, which would generally be considered as an indication that a calculational model reasonably represented the true surface.[11]

The above dilemma has been resolved by the assumption that the NiAl(111) surface consists of both domains of Al termination and domains of Ni termination. If the domains are sufficiently large, then electron diffraction from one domain does not coherently interfere with the diffraction from the other, and the total diffracted current at a detector is the sum of the intensities from the individual domains. The relative contributions to the sum from the Al- and Ni-terminated domains depend on the fractional surface areas of the two domains. As illustrated by Fig. 2, the assumption that the two coexist leads to a significantly improved agreement between calculated and experimental *I-V* spectra. To obtain the absolute minimum R_{ZJ} (the minimum of Fig. 2) over 400000 sets of calculated *I-V* spectra were considered in which Δd_{12} and Δd_{23} for both domains and the fractional mixture were varied. The result of the analysis is the indication that the NiAl(111) is a 50%-50% mixture of the

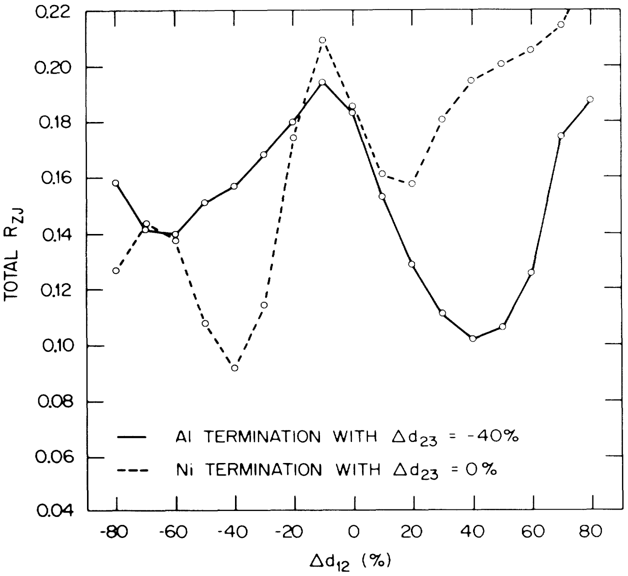

FIG. 1. Total R_{ZJ} as a function of first interlayer spacing for the Ni-terminated and Al-terminated surface, with second interlayer spacings fixed at the indicated values.

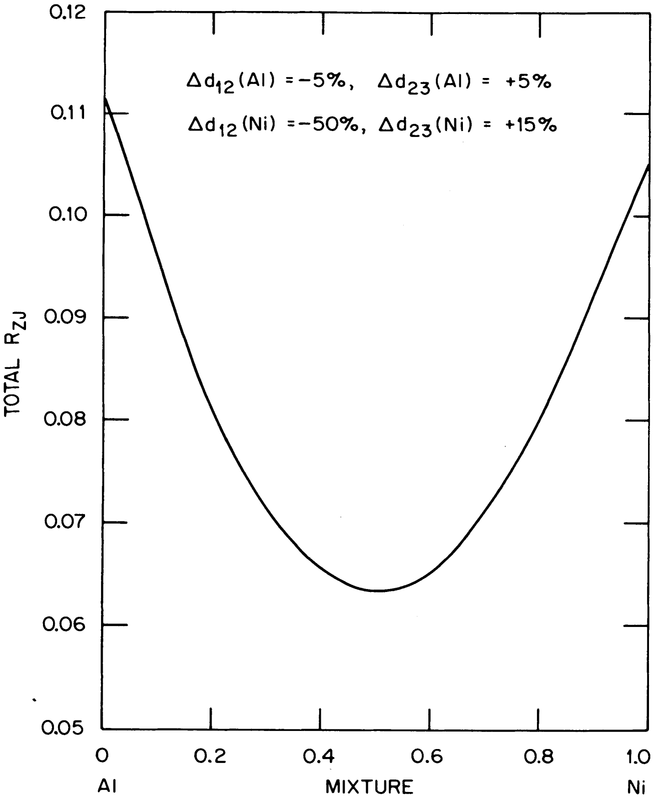

FIG. 2. Total R_{ZJ} vs mixture fraction of Al-terminated and Ni-terminated domains. This plot is for the indicated interlayer spacings of the two domains, which are those leading to minimal R_{ZJ}.

two ordered domains.

The minimum R_{ZJ} value of Fig. 2 is an ensemble minimum over the space of all the parameters which were varied. Thus, in addition to the analysis giving a strong indication that NiAl(111) is a 50%-50% mixture of Al-terminated and Ni-terminated domains, it has served to identify different multilayer relaxations in the two domains: $\Delta d_{12}(\text{Al}) = -5\%$, $\Delta d_{23}(\text{Al}) = +5\%$, $\Delta d_{12}(\text{Ni}) = -50\%$, and $\Delta d_{23}(\text{Ni}) = +15\%$.

Supporting evidence serves to strengthen the credibility of the structural model just discussed. Strong support comes from a visual inspection of the experimental and calculated *I-V* spectra, e.g., consider two of the seven beams analyzed as shown in Fig. 3. An inspection of spectra calculated for a model of an all Al-terminated surface, Al, and for an all Ni-terminated surface, Ni, with experimental spectra, EXPT, shows there are some peaks in the measured spectra that are missing in the "Al" spectra, or others missing in the "Ni" spectra. However, indications of all peaks in the experimental spectra are contained in the spectra for a 50%-50% mixture of both terminations, MIX. Evidence also is provided by beam-to-beam consistency. The agreement between calculated and experimental spectra is improved (R_{ZJ} lowered) significantly for five beams by use of the mixed-domain model rather than use of either of the single-termination models. For the two beams in which agreement was not improved (R_{ZJ} increased) by use of mixed domains, the agreement was not significantly degraded [see (0 1) frame of Fig. 3].

The R_{ZJ} and R_2 reliability factors weigh spectral features differently when each is used to compare experimental and calculated *I-V* spectra.[11,12] As a check on the above results, which were based on use of R_{ZJ}, the LEED analysis was repeated with R_2. This reanalysis produced about the same results—the NiAl(111) surface is a 50%-50% mixture of Al-terminated and Ni-terminated domains, and the multilayer relaxations of the respective domains agreed with the previous results to better than 3%.

The model for NiAl(111) that has emerged from the LEED analysis needs to be consistent with physical reali-

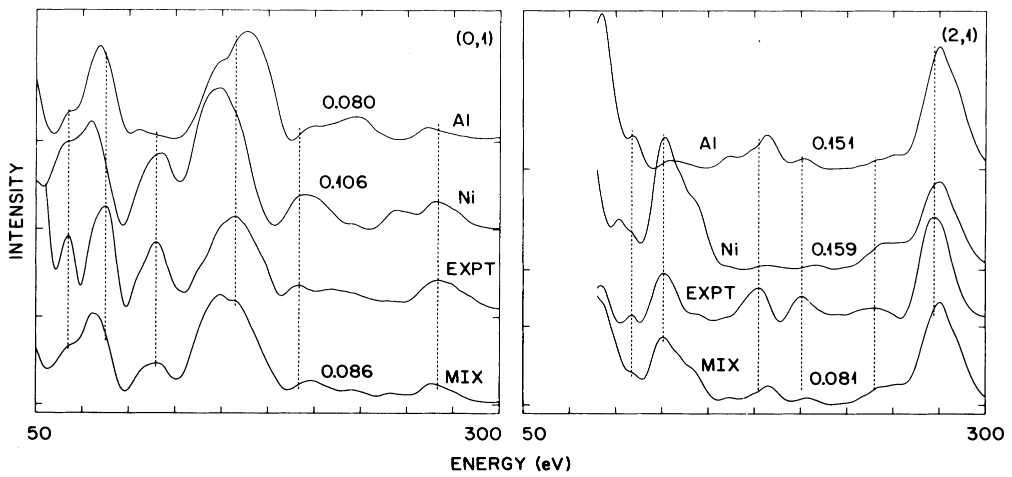

FIG. 3. *I-V* spectra for the (0 1) and (2 1) beams of NiAl(111).

ty. Needless to say, a NiAl single crystal with an atomically flat surface containing both Al- and Ni-terminated domains appears to be nonphysical. A more reasonable model is that of a surface with large terraces and steps with a single interplanar spacing between adjacent terraces. If the analysis had indicated that NiAl(111) was terminated by just a single type of atomic layer, then the terraces would have to be separated by steps of two interplanar spacings. The optimized R_{ZJ} value ($=0.063$) is consistent with the initial assumption that individual terraces of NiAl(111) are of sufficiently large area that any coherent interference between different terraces can be neglected. Since the agreement between experimental and calculated *I-V* spectra is not perfect, part of the disagreement may be caused by interference between terraces. But an $R_{ZJ}=0.063$ is comparable to values obtained in some of the more reliable LEED analyses that have been reported to date, which implies that interterrace interference is small.

The coexistence of a mixture of different terminations on the NiAl(111) surface was not expected initially. Although the coexistence of the two different terminations has been reported for the hcp (0001) surfaces of monatomic crystals,[13,14] previous studies of binary-alloy surfaces have indicated only a single termination when bulk crystallography suggests two possibilities.[1,3,5] The only difference between the hcp (0001) terminations is the cessation of a stacking sequence, and so the surface free energies of both terminations must be identical. Therefore, in equilibrium, there must be a 50%-50% mixture of both terminations. However, for binary alloys different surface structures would be expected to have different free energies, and in thermodynamical equilibrium one termination would be expected to dominate. Results previously reported[1,3,5] for Cu_3Au(100), Ni_3Al(100), and Ni_3Al(110) are consistent with this interpretation.

A possible explanation of why the NiAl(111) result is different from results for other binary-alloy surfaces is that the surface free energies of the two possible NiAl(111) terminations are comparable. Then domain-wall (single atom steps at terrace boundaries) energy can be the driving force. If the domain-wall energy is greater than the energy difference between the two terminations, a 50%-50% mixture of the terminations would be plausible. In fact, a recent total energy calculation[15] for the NiAl(111) surface indicates that the energy difference between the Al-terminated layer and the Ni-terminated layer is small, consistent with the model.

In conclusion, the existence of a novel crystallographic feature in the NiAl(111) surface has been indicated by an extensive LEED *I-V* analysis. Although previous work on binary-alloy surfaces in which two terminations are possible has always indicated that one termination predominates, the NiAl(111) surface contains a 50%-50% mixture of domains with the two possible terminations. This type of feature is probably not unique to NiAl(111). It is clear that this class of surface structure must be evaluated in analysis of the structure of metallic alloy surfaces. In addition, the results of the LEED analysis indicate that the interlayer relaxations are significantly different in the Al-terminated and Ni-terminated domains of NiAl(111). Such independent relaxations coexisting on a surface are reported here for the first time.

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