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Segregation-induced subsurface restructuring of FeAl(100)

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Upon sputtering and subsequent annealing, the subsurface region of the (100) surface of FeAl undergoes a transition to a practically stable and ordered Fe_3Al slab. It is capped by an Al top layer forming a rather complex interface to the bulk FeAl. This shows that routine surface preparation procedures with sputtering involved can lead to substantial restructuring extending deep into the surface. [S0163-1829(96)51732-7]

In substitutionally disordered binary alloys the phenomenon of segregation of one of the constituents to the surface usually leads to a layer-dependent deviation from the average bulk stoichiometry.[1,2] For chemically ordered alloys, however, this situation is rather rare and the corresponding surfaces in most cases exhibit bulk termination. Different elemental terminations of a surface can coexist in the case of chemically alternating layers. Exceptions result when the sample is prepared by ion bombardment with preferential sputtering of one of the constituents, in most cases depletion of the lighter elements. Subsequent annealing is generally believed to continuously restore the bulk stoichiometry as a consequence of diffusion, whereby nonstoichiometric phases may appear as intermediate structures. Frequently, the latter are substitutionally disordered or deviate from the ideal bulk in the top layer only. In the present paper, we report that—for a certain annealing temperature—the surface can also exhibit an *ordered structure that extends deep into the subsurface region* forming an interface to the bulk. The formation of metastable epitaxial films different from the bulk both in structure and stoichiometry is a well-known phenomenon when deposited material is thermally made to react. A prominent example is the evolution of silicide films on a silicon substrate after thermal processing of a metallic deposit. However, to our knowledge there is no report, nor has anyone even seemed to take into account yet, that such a process can take place simply upon moderate sputtering of an ordered compound surface.

In particular, we show that for the (100) surface of an ordered FeAl crystal an ordered and practically stable Fe_3Al phase develops. It is capped by a pure Al top layer, which might be interpreted either as the usual termination of the $Fe_3Al(100)$ surface or as a special feature of the interface to bulk FeAl. In any case the Al capping or termination confirms the trend for Al segregation as already found earlier for low index FeAl surfaces.[3] These findings—which are possibly not unique but, to our knowledge, up to now unobserved—are certainly relevant from the fundamental point of view and should be valuable information for scientists working in the field of multicomponent surfaces.

We present a surface structure determination by quantitative low-energy electron diffraction (LEED) of a FeAl(100) crystal surface prepared as described below. The sample's bulk stoichiometry was $Fe_{0.53}Al_{0.47}$ with bulk impurities of 50 ppm oxygen and carbon. Using x-ray diffraction the lattice constant was determined to be $a = 2.9030 \pm 0.0003$ Å at room temperature, in excellent agreement with the literature value.[4] After *ex situ* polishing of the surface (1 μm) its misorientation was below 0.3°. *In situ* Ar^+ ion bombardment (1 keV, 25 $\mu A/cm^2$, 20–30 min) resulted in a surface with impurities below the detection limit of Auger electron spectroscopy (AES). The latter also showed that upon sputtering the surface region is Al depleted on average to less than 30% in the first few layers and that subsequent annealing leads to diffusion of Al from the bulk towards the surface. The concentration of Al depends strongly on the annealing temperature and practically not on the annealing time, so that for each temperature applied some quasiequilibrium seems to be reached.[3]

At temperatures at or above 600 °C a sharp and low background 1×1 LEED pattern develops, which indicates that a well-ordered surface has been reestablished. In fact, results of a recent quantitative LEED analysis of this phase by Wang *et al.*[5] indicate an Al-terminated surface with contracted and expanded first- and second-layer distances, respectively, whereby a Pendry R factor[6] of $R_p = 0.36$ was achieved for the best theory-experiment fit. Our reanalysis of this phase ($R_p = 0.12$) confirms the layer relaxations ($d_{12} = 1.24 \pm 0.02$ Å, $d_{23} = 1.49 \pm 0.02$ Å, $d_{34} = 1.47 \pm 0.02$ Å, $d_{\mathrm{bulk}} = 1.4515$ Å) but, in addition to the 100% Al termination, finds about 20% enrichment of Al in the second layer. This permits the calibration of the Auger electron intensities and the precise determination of the necessary matrix factor. The latter was determined to be $F = 1.51$. Also, in view of the Auger electron energies (Fe: 47 eV; Al: 68 eV) an electron attenuation length of 4.2 Å was used consistent with values in the literature[7,8] and the optical potential used in the LEED analysis.

Following annealing at temperatures between about 350 and 410 °C a sharp $c(2\times2)$ superstructure develops. The annealing time was about 15 min but is uncritical: The $c(2\times2)$ superstructure persists even when annealing for hours in that temperature range. The same holds for lower temperatures once the superstructure is formed, i.e., the structure is practically stable, though metastable in the thermodynamic sense. For annealing at 400 °C the Auger electron intensities indicate an average Al concentration of $\hat{c}_{\mathrm{Al}}=0.55\pm0.07$ in the surface slab determined by the electron attenuation length. The $c(2\times2)$ structure remains stable at least for hours. However, the LEED intensity measurements were performed within a much shorter time in order to minimize adsorption of residual gas. The measurements were carried out at $T\approx-150$ °C and with normal incidence of the primary electron beam. An automated, video-based, and computer-controlled technique[9,10] was used to acquire intensity versus energy spectra, $I(E)$, which were recorded for seven integral and three fractional-order beams. The maximum energy was 500 eV and the total energy width for all beams amounted to 2426 eV. For the structural analysis, a maximum of 11 phase shifts for Fe and Al and 36 plane waves were used to describe the wave field. Layer diffraction matrices were calculated by matrix inversion and layers were stacked by the layer doubling scheme according to standard computer programs.[11]

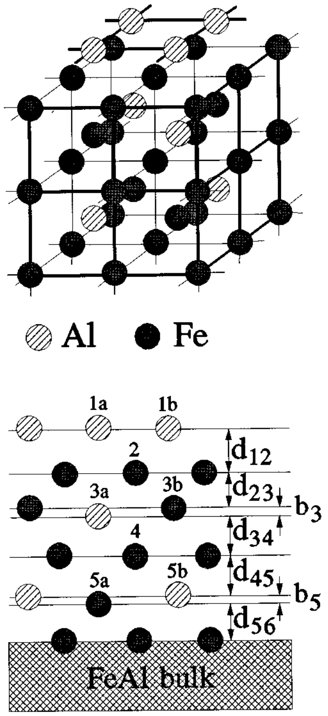

FIG. 1. Perspective view of the Al-covered Fe_3Al interface (top) and schematic cut through the surface along the [001] direction (bottom). The shaded area indicates the ideal FeAl bulk.

In a first attempt, we assumed the correct model for the observed superstructure to be characterized by a $c(2\times2)$ reconstruction in the top layer only. All reasonable models with $c(2\times2)$ arrangements of Al and Fe atoms as well as of vacancies with some additional vertical buckling were tested. Also, dimerization of atoms and substitutional disorder (also in deeper layers) were allowed. However, an R factor better than 0.55 was not obtained for any of the models and so they had to be eliminated. Instead, models with the superstructure extending deeper into the surface were considered, whereby a promising hint was obtained by inspection of the phase diagram of bulk FeAl.[12] An ordered Fe_3Al phase with atoms in the elementally mixed (100) layers arranged in a $c(2\times2)$ superstructure with respect to the arrangement in the elementally pure layers exist. Furthermore, the lattice misfit between FeAl and Fe_3Al is only 0.5%,[4] so that an interfacial Fe_3Al slab may easily form on top of the bulk FeAl phase. In order to account for the observed Auger intensities, the surface was assumed to be capped by an Al layer. This has been determined in a recent low-energy ion scattering investigation of similarly prepared samples.[13] Therefore, we tested models as displayed in Fig. 1 with—below the top Al layer—alternating pure Fe and mixed Fe-Al layers according to the Fe_3Al structure. The shaded area in the bottom panel indicates the ideal FeAl bulk. As demonstrated by the R-factor behavior in Fig. 2, there is a continuous improvement of the theory-experiment fit with the number of Fe_3Al layers in the interface whereby interlayer distances are optimized for each point. As judged by the variance of the R factor,[6] at least six Fe_3Al layers must exist, but a higher number is probable as indicated by the further decrease of the R factor. Of course, this uncertainty is due to the limited penetration of low-energy electrons. We emphasize that less than four layers of Fe_3Al results in a substantially higher R factor. Also, it is important to mention that the model with four or more Fe_3Al layers including the Al top layer yields an average Al concentration of $\hat{c}=0.49$ within the surface slab limited by electron attenuation. This, within the limits of errors, agrees with the experimental value of 0.55 ± 0.07 determined by Auger electron spectroscopy.

For further structural refinement, we assumed the Fe_3Al interface to be much thicker than the electron attenuation length, i.e., practically unlimited as supported by the R-factor behavior. The refinement is necessary since a surface reconstruction consistent with the observed $c(2\times2)$ superstructure may be present. This reconstruction may be purely geometric, e.g., vertical buckling of inequivalent atoms in mixed layers as indicated by the rippling displayed in the model in Fig. 1. Additionally, substitutional disorder might result from an incomplete ordering process. Substitution in the top Al layer may also be induced by the different chemical nature of next nearest neighbors in the third layer. Therefore, a different stoichiometry might result for atoms at positions $1a$ and $1b$ (which in turn may lead to some buckling in this layer). In principle this holds also for atoms labeled $3a,b$ and $5a,b$. Thus, for layers 1, 3, and 5 the occu-

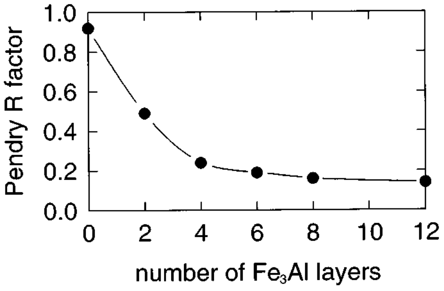

FIG. 2. Pendry R-factor behavior as a function of the number of layers in the Fe_3Al interface.

pation of two different sites has to be determined, while for layers 2 and 4 the determination of the average stoichiometry is sufficient. A perfect tool to retrieve such deviations from the above described ideal and Al-capped Fe_3Al structure, which we view as a reference structure in the following, is *Tensor LEED*. Its original version, to determine geometrical atomic displacements from a reference,[14,15] has been recently extended to the retrieval of chemical substitutions and thermal vibrations,[16–18] a combination well suited for the present case. In addition to interlayer distances $d_{i,i+1}$ ($i \leqslant 5$), buckling amplitudes b_i ($i=1,3,5$) need to be determined, amounting to a total of eight geometrical parameters. Moreover, there is the stoichiometry $c_{ia,b}$ of two sites a,b in layers $i=1,3,5$ and the average stoichiometry c_i in layers $i=2,4$ amounting to another eight chemical parameters. Variation of vibrational amplitudes of the capping Al atoms and of subsurface Fe and Al atoms provide three additional parameters. This amounts to a total of 19 parameters. A simulated annealinglike automated search procedure[18,19] was applied to determine these parameters. The best fit gives an R factor $R_p=0.144$ and a variance $var(R_p)=0.0218$. The result for the interlayer distances with respect to the center of mass planes is $d_{12}=1.255\pm0.025$ Å, $d_{23}=1.490\pm0.020$ Å, $d_{34}=1.445\pm0.020$ Å, $d_{45}=d_{56}=1.447\pm0.026$ Å compared to the bulk value $d_b=1.447$ Å. The buckling amplitudes are $b_1=0.00\pm0.03$ Å, $b_3=0.08\pm0.03$ Å, and $b_5=-0.03\pm0.03$ Å with the iron atom up (down) in the third (fifth) layer. Within the limits of error given by the R-factor variance the surface stoichiometry is practically unchanged with respect to the reference given in the lower panel of Fig. 1, though the best fit indicates some modified concentrations, namely, $c_{1a}=87\pm12\%$ Al, $c_{1b}=100\pm20\%$ Al, $c_2=90\pm12\%$ Fe, $c_{3a}=100\pm13\%$ Al, $c_{3b}=100\pm13\%$ Fe, $c_4=100\pm12\%$ Fe, and $c_{5a}=100\pm16\%$ Fe, $c_{5b}=100\pm16\%$ Al. Top-layer Al atoms were found to vibrate with an average amplitude of 0.15 ± 0.06 Å, while the amplitudes of subsurface atoms were determined to be 0.10 ± 0.05 Å for Fe and 0.08 ± 0.07 Å for Al. Apart from the low minimum R-factor level achieved, the good quality of the fit appears also by visual comparison of calculated and experimental spectra as given in Fig. 3 for two selected beams.

With respect to the interlayer distances $d_{i,i+1}$ the above results are in good agreement with the values obtained for the FeAl(100) 1×1 phase. The large first interlayer contraction is of the order of that observed for bcc(100) surfaces. Concerning the concentrations, the values for the 3rd, 4th, and 5th layers correspond to those of Fe_3Al bulk. In contrast, the top layer is almost pure Al. In other words, if one views this top layer as a mixed Fe_3Al layer, there is extensive Al segregation at Fe positions. This Al segregation in the top layer and the much smaller segregation in the second layer is in qualitative agreement with the properties observed for the 1×1 phase. The chemical homogeneity of the top layer is probably responsible for the fact that no rippling is observed in this layer. However, it leads to different pairs of next nearest-neighbor atoms in the first and third layers, i.e., Al-Al ($c_{1a}-c_{3a}$) and Al-Fe ($c_{1b}-c_{3b}$) pairs. This is interpreted to cause the observed buckling in the third layer and by protrusion into the surface with less amplitude also in the fifth layer, eventually decaying for deeper layers.

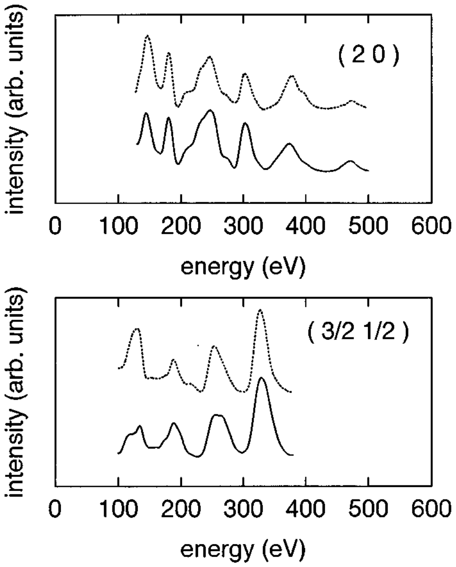

FIG. 3. Comparison of measured (bottom lines) and calculated best fit spectra for the (20) and $(\frac{3}{2},\frac{1}{2})$ beams.

As described, the structure determination identifies a vertically extended slab of Fe_3Al on top of FeAl of at least 6 but probably more layers in thickness. This seems to be a practically stable interface formed at the annealing temperature of about 400 °C. Since it would be interesting to know more about the stoichiometric behavior of the surface upon annealing, we monitored the Auger electron intensities as function of temperature. Ten minutes were given at each temperature to establish equilibrium (or at least quasiequilibrium) with practically constant intensities. From the knowledge of the surface being capped by an Al layer that holds generally for temperatures above 300 °C (Ref. 13) and by using the predetermined matrix factor, we calculated the average aluminum concentration in the accessed subsurface slab as function of temperature. The resulting data and a curve drawn through them are displayed in Fig. 4 and inserted into the iron-rich section of the FeAl phase diagram taken from Ref. 12. The temperature range within which the $c(2\times2)$ super-

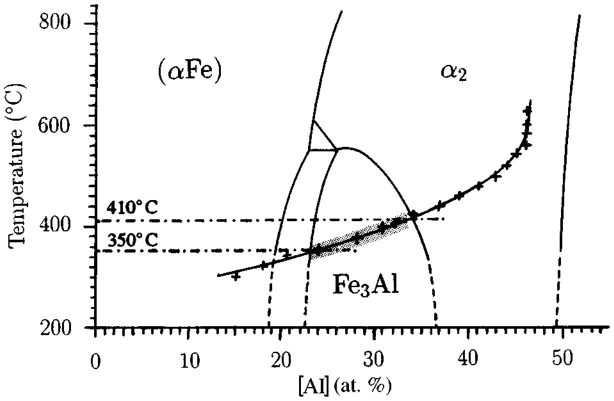

FIG. 4. Stoichiometry of the presputtered FeAl surface for various annealing temperatures (crosses) inserted into a section of the FeAl phase diagram taken from Ref. 12. The shaded part of the curve indicates the region in which the $c(2\times2)$ superstructure is observed.

structure is observed, i.e., between 350 and 410 °C as mentioned above, is additionally shaded. Obviously, the range almost ideally coincides with the stability range of Fe_3Al. As described in the literature,[20–22] up to about 22 at. % Al, the occupation of the lattice sites is statistical. With increasing Al concentration, the occupation is preferential and forms the Fe_3Al lattice whose ideal stoichiometry is for 25 at. % Al with alternating pure Fe and mixed Fe-Al layers. Beyond 25 at. % Al, more Al atoms substitute for Fe atoms in mixed layers until at about 50 at. % alternating pure Fe and Al layers order in the ideal FeAl lattice. Our measurements nicely correlate with this behavior. In particular, they show that the transition to FeAl upon annealing takes place via temperature controlled stoichiometric changes in a finite surface slab according to the volume phase diagram and *not* via, e.g., a layerwise growth of FeAl from the substrate interface towards the very surface. However, we should emphasize that the underlying diffusion/segregation processes are rather complex as indicated by the formation of a pure Al top layer despite the Al depletion in the subsurface region.

In conclusion, we have demonstrated that after sputtering and subsequent annealing to about 400 °C the ordered FeAl(100) surface forms a practically stable and ordered interfacial Fe_3Al phase extending deep into the surface. It is sandwiched by a pure Al top layer and the FeAl bulk. Similar transitions to a new chemical structure in an extended surface slab upon sputtering might also happen in other compound surfaces though this has not yet been reported.

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