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Interaction of hydrogen and deuterium with CoTi surfaces

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The interaction of H_2 and D_2 with polycrystalline CoTi in the annealed and unannealed states, and at 300 and 80 K, has been studied using ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy, electron-energy-loss spectroscopy (EELS), thermal desorption spectroscopy, and measurement of work function. The two surface conditions, annealed and unannealed, were found to be slightly enriched in Ti and Co, respectively. Both H_2 and D_2 were found to react readily with CoTi at both 300 and 80 K, causing changes in the UPS spectra that could be explained from density-of-states calculations on CoTi and (by extension) on $FeTiH_x$. The surface stoichiometry was unaltered by the interaction, indicating no adsorbate-induced segregation, and there was no evidence from EELS of the formation of a separate hydride phase. However, EELS was able to demonstrate the presence of H_2 or D_2 at the surface by virtue of the rapid quenching of a surface loss feature on initial exposure. On heating above ≈ 500 K H_2 or D_2 were desorbed, the desorption threshold temperature increasing progressively with successive cycles of heating. For both H_2 and D_2 interaction the work function increased on exposure, but reached different saturation levels at 300 and 80 K, respectively. All these results are consistent with a mechanism of H_2 or D_2 chemisorption followed by inward diffusion and the formation of an α-phase solid solution, but not with formation of a hydride phase.

I. INTRODUCTION

The elements Ti, Fe, and Co form a pseudobinary alloy system where the two binary phases FeTi and CoTi and the substitutional pseudobinary alloys $Ti(FeCo_{1-x})$ all crystallize in the CsCl structure. FeTi is a well-known hydride-forming intermetallic compound with major technological and considerable academic interest.[1,2] The hydrides $FeTiH_x$ ($x=1-2$) are of intermediate stability as judged by their heat of formation of 13–15 $kJ\,(mol\,H)^{-1}$, and as such well within the range of hydrides considered suitable for hydrogen storage purposes.[3] However, unlike many other intermetallic compounds FeTi needs to be activated to absorb hydrogen in significant quantities, the activation procedure consisting of heat treatments at $T>670$ K in vacuum or in hydrogen atmosphere.[4] Numerous papers on the activation procedure of FeTi, and almost as many hypotheses on the most important reaction step of the activation process, have appeared in the literature.[5] It appears that the destruction of passivating oxide layers, surface segregation phenomena, and the bulk properties of the virgin samples, such as H diffusion and fracture toughness, play important roles. The electronic structure of FeTi hydrides has been investigated theoretically by Gupta[6] and Papaconstantopoulos and Switendick,[7] and we will refer to some aspects of these calculations later in this paper. The bulk band structure of FeTi has been probed experimentally using photoelectron spectroscopy by Weaver and Peterson,[8] and the experimental data compare reasonably well with band-structure calculations of Yamashita and Asano[9] and Papaconstantopoulos.[10]

Whereas FeTi appears to be rather popular in metal-hydride-related research,[2,11] little attention has been paid to CoTi which is akin to FeTi in both geometric and electronic structure. Indeed, the densities of states (DOS) of FeTi and CoTi are very similar as revealed by the comparative calculations of Schadler and Weinberger[12] and of Eibler *et al.*;[13] the major difference is in the position of the Fermi level, which is moved upwards to a region of higher DOS in CoTi compared to FeTi, because an extra electron has to be accommodated. The heat of formation of CoTi hydride is of the order 10–13 $kJ\,(mol\,H)^{-1}$,[3] which classifies CoTi as a potential H storage material.

As part of a program to investigate the initial stages of hydride formation[14] we have studied in the present work the interaction of hydrogen and deuterium with clean, chemically well characterized, surfaces of CoTi under ultrahigh-vacuum (UHV) conditions. A number of surface-sensitive techniques including uv photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), electron-energy-loss spectroscopy (EELS), thermal desorption spectroscopy (TDS), and work-function measurements have been combined to characterize the first stages of hydrogen and deuterium interaction with CoTi at room and at low temperature.

We find that H_2 and D_2 react readily with clean ordered and disordered polycrystalline surfaces of CoTi, at 300 K as well as at 80 K. No surface hydride phase appears to be stable on CoTi in an UHV environment, but the data indicate that besides chemisorbed hydrogen a solid solution α phase of variable composition is being formed.

II. EXPERIMENT

The experiments were carried out in an angle resolving electron spectrometer (VG ADES 400) with facilities for UPS, AES, EELS, low-energy electron diffraction (LEED), and with the usual provisions for sample manipulation and cleaning. The background pressure in the system was $< 10^{-10}$ mbar. Thermal desorption of gases was monitored in a mass spectrometer, which was arranged in line of sight of the sample surface. Photoelectrons were excited by He I ($h\nu=21.2$ eV) radiation and analyzed in normal emission with an analyzer energy resolution of 180 meV and an angular resolution of ±1°. Electron-energy-loss spectra were measured in specular reflection geometry with angle of incidence 42.5° with respect to the surface normal; the full width at half maximum of the elastically reflected peak was 400–500 meV. Sample work functions were derived from the width of the electron energy distribution curves of photoemitted electrons with an accuracy of ±25 meV.

The sample, a disc of CoTi of ≈ 1 mm thickness, fabricated by Metal Crystals, Cambridge, UK, was clamped onto a thin Ta holder, which in turn was attached to the sample manipulator. The Ta holder could be heated resistively and cooled from 300 to 80 K within 10 min. The CoTi sample was originally a single crystal oriented to expose a (110) surface, but in the course of *in situ* surface cleaning by alternate cycles of Ar^+-ion bombardment (1–2 keV) and annealing in vacuum up to 1200 K, the surface became faceted and rough as revealed by LEED, resulting in a sample surface which was atomically clean but essentially characteristic of polycrystalline material. The sample surfaces used in the present investigation were free of surface impurities with the exception of small amounts of oxygen on the annealed surfaces, which segregated as a bulk impurity to the surface during heating, as described in the next section.

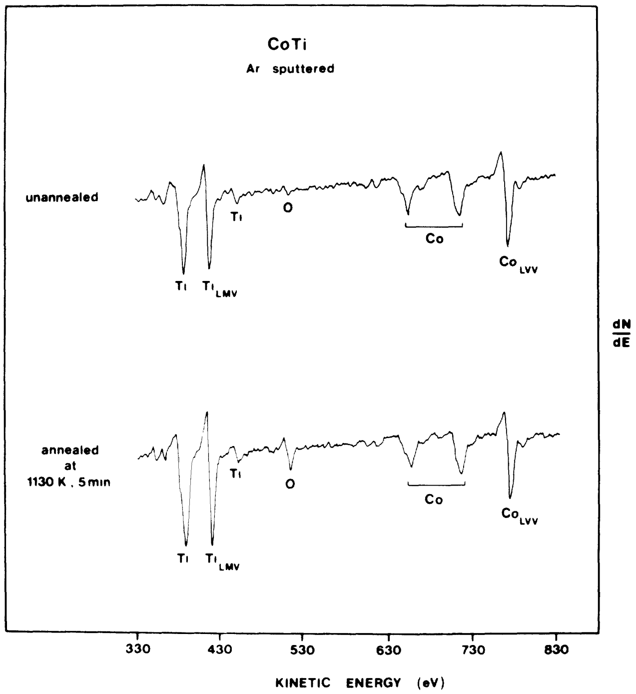

FIG. 1. Auger spectra of sputtered CoTi surfaces (1 keV Ar^+, 30 min, ~10 μA) before and after annealing to 1130 K.

III. RESULTS

A. Characterization of CoTi Surfaces

Surface segregation phenomena are well known in intermetallic compounds,[15,16] and the surface of the CoTi had to be characterized first in chemical and electronic terms to establish a basis for subsequent gas exposure experiments. Figure 1 shows Auger spectra of the Ar-bombarded CoTi surface before and after annealing to 1130 K. The Co-to-Ti atomic ratio was determined by using first the Ti *LMV* and Co *LVV* Auger transitions and a peak-to-peak sensitivity factor of 2 for bulk Ti with respect to bulk Co, which is a mean value of those given in the literature.[17,18] After application of this sensitivity factor, account was taken of the different inelastic mean free paths corresponding to the two Auger transition energies by using the value 0.75 for the exponent m in the relationship $\lambda = kE^m$. This value was shown by Powell[19] to be the average of the various semiempirical and experimental determinations of m made subsequent to the empirical derivation of Seah and Dench,[20] who found $m=0.5$. Powell and co-workers have also recently[21] derived a Bethe-type expression in which λ is a function of $E/\ln E$; if their expression is used with the known[1] density of CoTi, then the Ti *LMV* to Co *LVV* inelastic mean-free-path ratio is exactly the same as using $m=0.75$. The atomic concentrations so found for the CoTi surface at various stages are given in Table I. The Ar-bombarded, unannealed surface was slightly Co-rich as revealed by a [Co]/[Ti] ratio of 1.17, presumably as a result of preferential sputtering of Ti, and contained a trace of oxygen. Annealing induced some slight Ti surface segregation, since after 5 min at 1000 K the [Co]/[Ti] ratio dropped to 1.12, and at the same time O segregated into the surface region from the bulk as evidenced by the increase in the O concentration from 4.3 to 11.9 at. %. Annealing at 1130 K reduced the [Co]/[Ti] ratio further until the surface became slightly Ti-rich (0.86), and also caused a further slight O segregation. In fact, it was never possible to obtain annealed CoTi surfaces completely free of oxygen. However, the oxygen concentrations quoted in Table I must be regarded as upper limits as far as the external surface is concerned, since the oxygen signal would have been distributed over the escape depth corresponding to the Ti *LMV* kinetic energy (≈ 420 eV) (to which all the Auger signals have been normalized), as a result of diffusion from the bulk. The interaction of oxygen with CoTi will be the subject of another paper,[22] but it is relevant to mention here that AES and EELS data suggest that the oxygen atoms are associated with the Ti

TABLE I. Surface composition of Ar sputtered CoTi surfaces as a function of annealing, at. %.

Condition	Co	Ti	O	C	[Co]/[Ti]
Unannealed	51.6	44.1	4.3	0	1.17
1000 K, 5 min	46.5	41.6	11.9	0	1.12
1130 K, 5 min	40.1	46.7	13.2	0	0.86

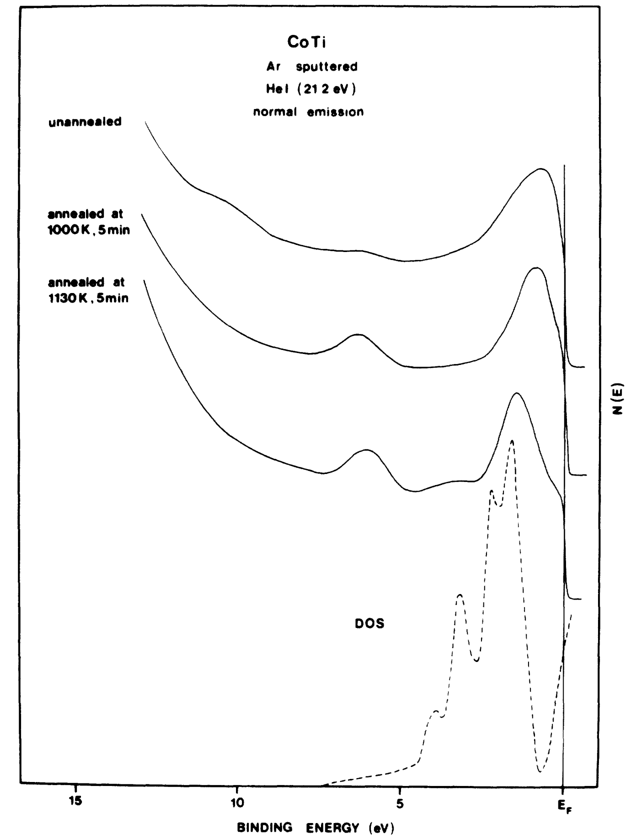

FIG. 2. Photoemission spectra of unannealed and annealed CoTi surfaces. The spectra are compared to a density-of-states calculation (dashed) (Refs. 12 and 13).

atoms.

The changes in the electronic structure of CoTi as a result of annealing and ordering were probed by UPS as shown in Fig. 2. The Ar-bombarded, unannealed surface had a broad density-of-states structure between E_F and 4 eV below E_F, peaking at ≈ 1 eV (top curve, Fig. 2). Introduction of surface order by annealing induced more structure in the DOS, with the main peak sharpening and shifting away from the Fermi level to higher binding energy. This could be seen in UPS after 1000-K annealing, and became more pronounced after annealing at 1130 K, where the DOS structures were better defined. O surface segregation during annealing was observable in UPS as a feature at ≈ 6 eV.

Comparison of the UPS spectrum of the annealed surface with a calculated total DOS of CoTi (Refs. 12 and 13) reveals good agreement between experimental and theoretical curves (Fig. 2): the main DOS peak and the higher-energy features around 3–4 eV are well reproduced in the calculations, and the valley in the theoretical DOS just below E_F is also indicated in the data. Comparison of the normal emission spectra with a total DOS is justified here, because the measured spectra correspond in fact to those taken under angle-averaged conditions as a result of the largely polycrystalline nature of the surface. Surface disorder tends to smear out DOS structures and in particular to fill up the DOS valley below E_F as seen in the UPS spectrum of the unannealed surface. Such behavior is also expected on theoretical grounds.[9]

In the next section the interaction of hydrogen and deuterium with both unannealed, disordered, and annealed, microscopically ordered, surfaces of CoTi of polycrystalline character will be described. It should be borne in mind that the annealed surface was slightly Ti-rich and with a small oxygen impurity content, while the unannealed surface was slightly Co-rich but with very little oxygen. Carbon did not reappear once it had been removed in the early stages of cleaning.

B. Interaction of CoTi with H_2 and D_2

A set of UPS spectra of the unannealed surface recorded after different H_2 exposures at 300 K is shown in Fig. 3. H_2 exposure resulted in increased emission near the main DOS structure and in the region 4–9 eV, and these H-induced emissions increased in intensity with increas-

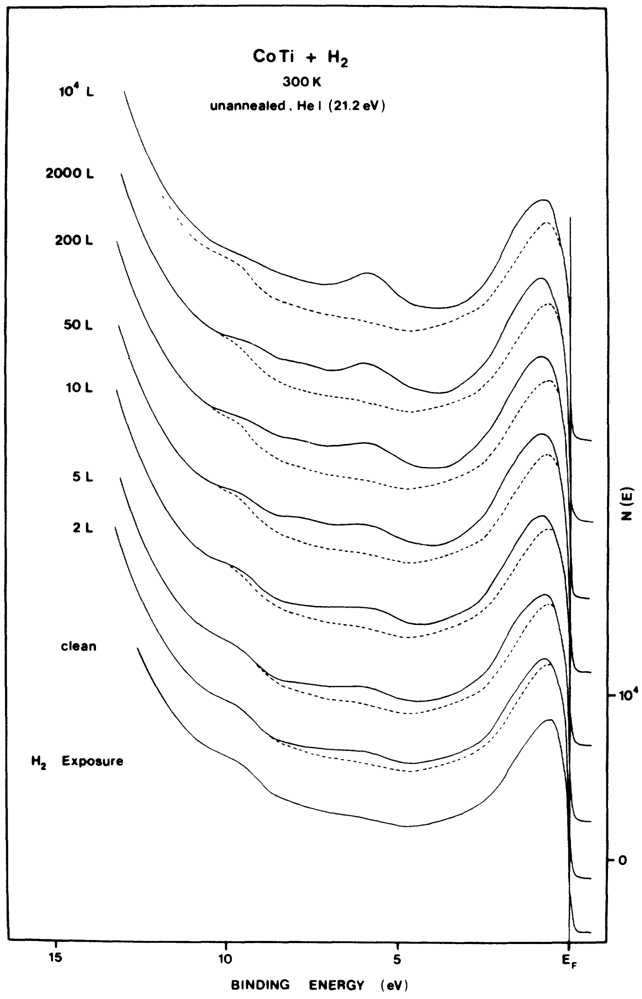

FIG. 3. Photoemission spectra of unannealed CoTi exposed to H_2 at 300 K. Exposures are given in langmuirs (1 L$=10^{-6}$ torr sec). The dashed curves represent the clean surface contribution.

ing hydrogen dose. After 10^4 L H_2 [1 langmuir (L)$=10^6$ torr sec]a peak was clearly visible at 5.5–6 eV, and increased background emission compared to that from the clean surface was observed between 1 and 10 eV. At this point AES revealed no contamination signals, so that attribution of the UPS spectral changes to the influence of H is permissible. AES analysis after high H_2 doses showed that the surface composition, that is the [Co]/[Ti] ratio, remained unaltered. H-induced surface segregation was therefore negligible. The H-induced spectral changes in UPS may be emphasized by the use of difference spectra, i.e., H_2 exposed minus clean spectra, and such a set of difference spectra corresponding to Fig. 3 is displayed in Fig. 4. We notice a peak at ≈ 1.5 eV and broad structure between 4 and 7 eV at low H_2 doses, but the development of two maxima at 5.8 and 8.0 eV at higher H_2 exposures. The weak feature at ~ 7 eV at low H_2 exposures appeared to shift to 8 eV at progressively higher H concentrations.

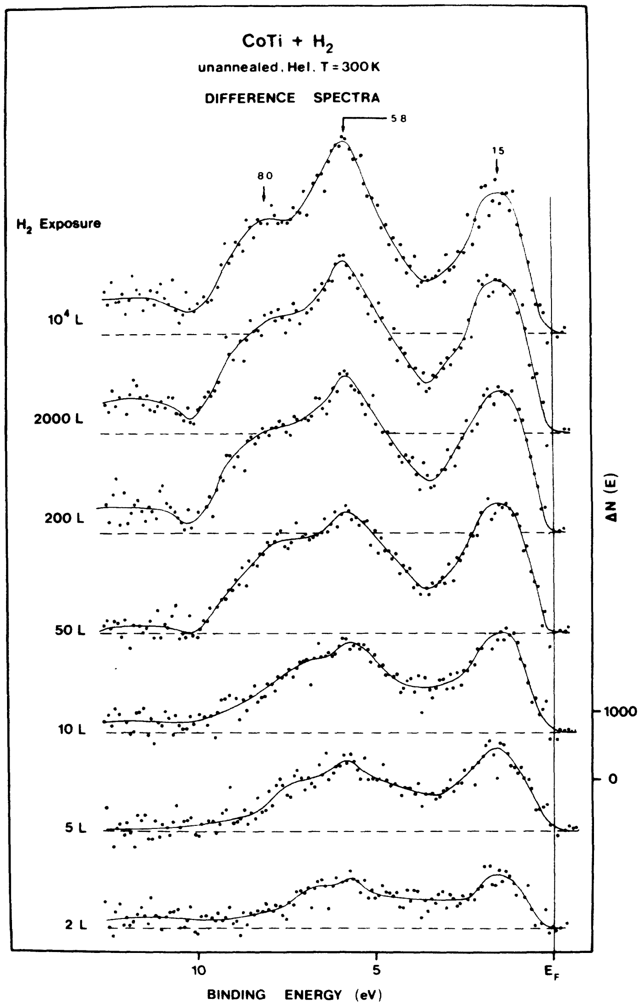

FIG. 4. Photoemission difference spectra, H_2-covered minus clean, corresponding to the set of spectra in Fig. 3. The dots represent the raw data, the solid lines the data subjected to a nine-point smoothing routine.

In Fig. 5 the effects of H_2 uptake at 300 K on the annealed surface as reflected in UPS are shown. The annealed surface showed more distinct DOS structure, as remarked above, and also some emission from O contamination at ≈ 6 eV. Exposure to H_2 increased emission around 1–2 eV and in the region 4–8, but the H-induced effects appeared to be less pronounced than on the unannealed surface. This is confirmed by the difference spectra included in Fig. 5, in which H-derived structures on the annealed and the unannealed surfaces are compared directly. On the annealed surface features were observed at 1.7 eV and around 5.5 eV, but the major differences between the ordered and the disordered surfaces appeared to be those of relative intensity. The annealed surface was clearly less reactive than the unannealed.

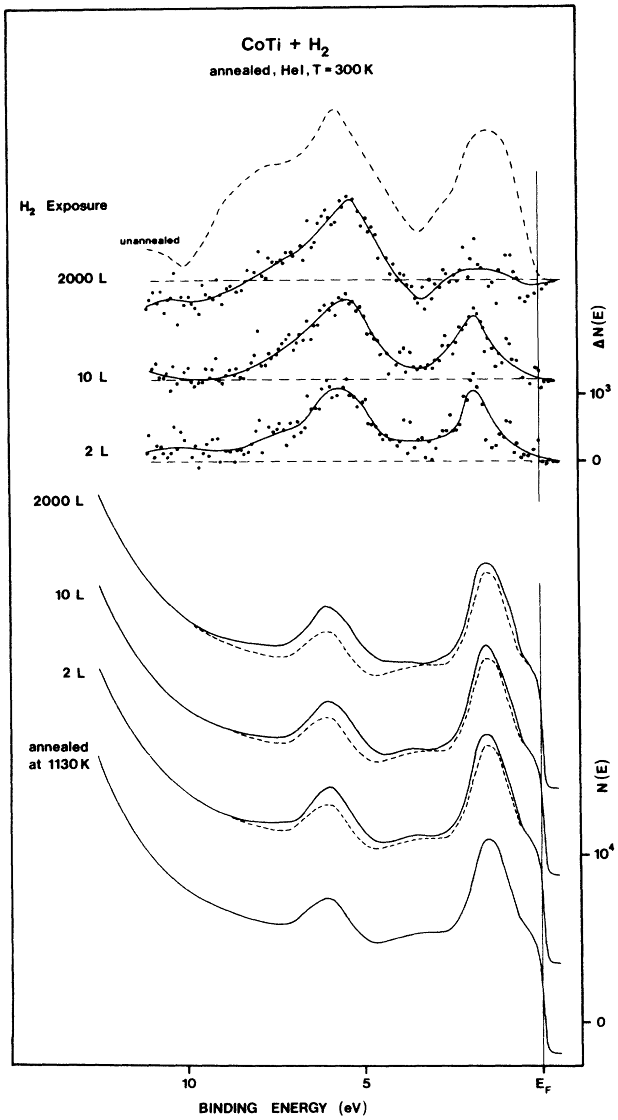

FIG. 5. Photoemission spectra of annealed CoTi exposed to H_2 at 300 K, integral (below) and difference (above) spectra. Note that the feature around 6 eV on the unexposed surface is due to oxygen contamination segregated from the bulk. On top of the figure a difference spectrum from the unannealed surface (dash-dotted line) is included for comparison.

Exposure of the unannealed CoTi surface to H_2 and D_2 at *low* temperature, 80 K, gave rise to the UPS difference spectra in Fig. 6. We note again H-derived structures at 1–2 and 4–9 eV; the structures between 4 and 9 eV consisted in this case of two maxima of roughly equal intensity at 5.5 and ~8 eV. Clearly, the UPS emissions of D closely parallel those of H. Comparison of the spectra obtained at 80 K with those at 300 K (dashed curve in Fig. 6) reveals a similar appearance in general, but quantitative differences in intensity and detailed shape.

Electron-energy-loss spectroscopy has proved very suitable for the detection of the advent of hydride phases in rare-earth systems, via characteristic hydride-related plasmon excitations.[14] In Fig. 7 are shown EELS spectra representative of H_2- and D_2-exposed unannealed CoTi surfaces, using a primary electron energy of $\approx$250 eV. The bottom curve shows the EELS spectrum of the clean, disordered surface. The annealed surfaces of CoTi (not shown in Fig. 7) had a somewhat more pronounced structure at 10–13 eV and around 20 eV, but in general similar excitation profiles. H_2 or D_2 exposure reduced the loss intensity around 10 eV in all cases, confirming the surface origin of the loss features in this region; the most likely interpretation is that of a surface plasmon excitation, which becomes suppressed by H_2 or D_2 uptake at the surface. However, no additional loss features or shifts of loss peaks of the clean surface were observed, which would have indicated the formation of a surface hydride phase. Note that the formation of hydride phases is usually accompanied by the appearance of characteristic hydride plasmons, with the hydride bulk plasmons at higher loss energy than the corresponding metal plasmons.[23–25] Thus, no indication of the nucleation of surface hydrides can be derived from the present EELS investigation. The loss curves in Fig. 7 refer to exposures needed to saturate the surface plasmon depression. These were 50–100 L for H_2 at 300 K, but only 5–10 L at 80 K. At 80 K surface-to-bulk transfer was obviously slowed down, and saturation of the surface H or D population was reached at lower exposures. The top curve in Fig. 7 shows that the surface-sensitive loss peak could be restored by heating the H_2-exposed surface to 600 K.

The work function of CoTi was also measured as a function of H_2 and D_2 exposure at 300 and at 80 K. The clean, unannealed surface was characterized by a work

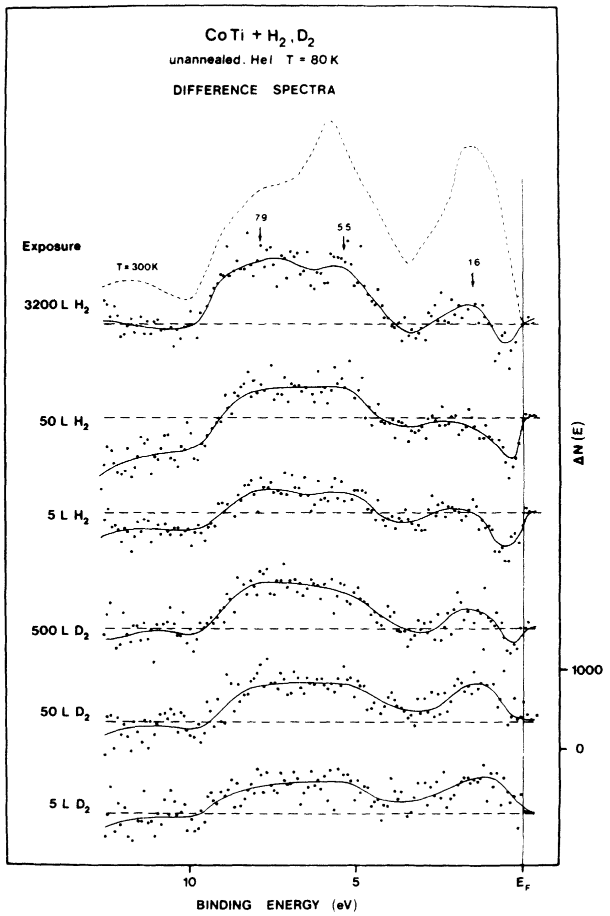

FIG. 6. Photoemission difference spectra of the unannealed CoTi surface, exposed to H_2 and D_2 at 80 K. The dashed curve on top is a corresponding difference spectrum obtained after H_2 exposure at 300 K.

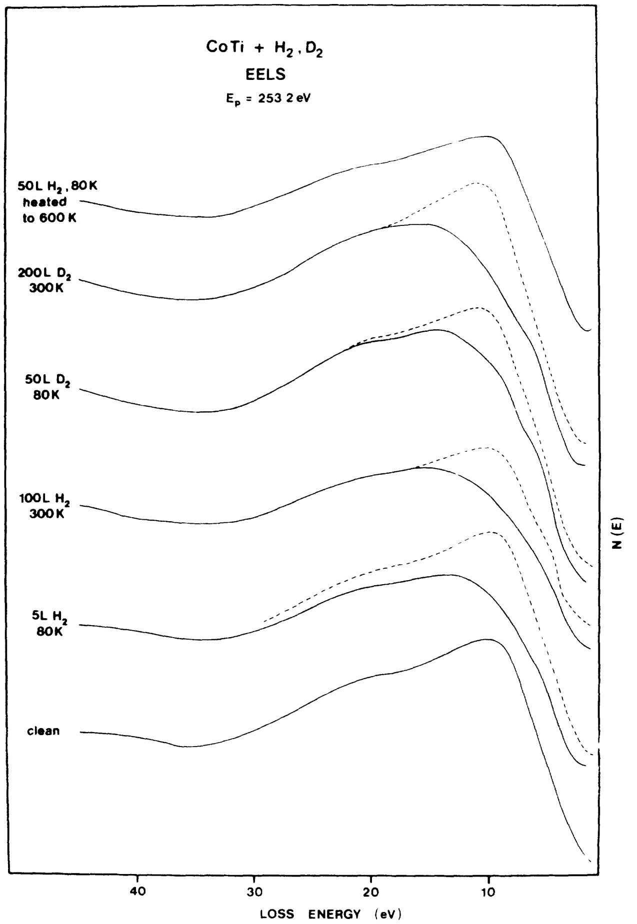

FIG. 7. Electron-energy-loss spectra of unannealed CoTi exposed to H_2 and D_2 as indicated. The dashed curves represent the corresponding clean surface spectra.

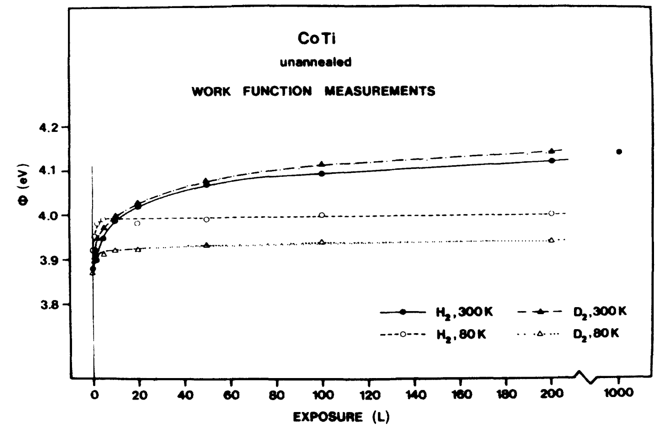

FIG. 8. Work-function change of CoTi as a result of H_2 and D_2 exposure at 300 and at 80 K.

function of 3.9±0.025 eV. H_2 (D_2) exposure increased the work function in all cases as seen in Fig. 8, but the rate of change and the saturation values after 1000 L exposure were different at 80 and at 300 K, for H_2 and for D_2. A work-function increase at the initial stages of a hydrogen-solid interaction indicates that charge is being transferred from metal atoms to the hydrogen atoms at the surface. The different saturation values obtained for the different experimental conditions suggest that surface layers of different structure and/or stoichiometry were being formed.

Desorption of H_2 or D_2 from CoTi was initiated by heating the H_2- (D_2-) exposed sample to >500 K. H_2 (D_2) evolved from the surface in large quantities after high exposures, and subsequent heating cycles without fresh exposure gave desorption signals every time, whose threshold shifted to progressively higher temperatures. Such behavior cannot be accounted for by desorption from a simple adsorbate layer, but is characteristic of the decomposition of a solid solution phase.

IV. DISCUSSION

In the following discussion we will focus on the changes in the electronic structure of CoTi as a result of hydrogen uptake and combine with them supporting evidence for the formation of a solid solution phase. The electronic structure of CoTi is similar to that of FeTi as shown by the calculation of Schadler and Weinberger[12] and of Eibler *et al.*[13] In the absence of calculations on CoTi hydrides it appears appropriate therefore to use the calculations on FeTi hydrides[6,7] to guide the present discussion. As pointed out by Gupta[6] and Papaconstantopoulos and Switendick[7] H 1*s* states combine with metal states of predominantly Fe *d* character to form the so-called "bonding bands" below the metal *d* bands. The H-induced UPS structures at 4–9 eV in CoTi are most likely to be associated with these bonding bands, and it is assumed that Co provides the major *d* contribution to these bands, in analogy to Fe in $FeTiH_x$. The deep-lying metal-hydrogen bands are formed from states which are already filled in the pure intermetallic compound. The above-mentioned calculations[6] indicate that in addition metal *p* states from 1.5 eV above the Fermi level are lowered by ≈ 3 eV by the metal-hydrogen interaction and brought inside the metal *d* bands below E_F. These changes appear to be reflected in the present UPS results, since the structures observed 1.5–2 eV below E_F are in very good agreement with the theoretical predictions. For $FeTiH_x$ the calculations show a DOS increase at the Fermi level, due to an upward shift of the Fermi level as a result of additional charge being transferred from H to the metal. This DOS increase at E_F is not observed in the present UPS spectra although a similar shift of the Fermi level would be expected in the transition from CoTi to $CoTiH_x$. The absence of this Fermi-level shift may be explicable by the fact that no actual hydride phase is formed under present experimental conditions, but that only a low-concentration solid solution phase is reached. If the H concentration in this α phase is sufficiently low, the shift of the Fermi level may not be experimentally observable, as, according to the calculations, the Fermi-level shift is dependent on the H concentration.[7]

The lack of surface hydride formation on CoTi in UHV environment indicates that CoTi hydrides are unstable under these conditions. This is to be expected on thermodynamic grounds since the dissociation pressure P_{H_2} estimated from the heat of formation of the hydride[3] is $> 10^{-3}$ mbar at 80 K. The experiments with D_2 at 80 K confirm that bulk diffusion is not an important factor in diluting the hydrogen concentration in the surface region: bulk diffusion should be sufficiently slow for D at 80 K to allow surface hydride nucleation. At 80 K the H (D) surface saturation concentration is reached at much lower exposures than at 300 K (see Figs. 7 and 8). This may be the result of a kinetic limitation on surface-to-bulk penetration, in the spirit of the surface barrier model of Pick *et al.*,[26] in which the rate constants for such a penetration are temperature dependent.

The formation of a solid solution α phase is consistent with all the experimental observations. The quantitative differences between the H-induced UPS structures at 300 and 80 K, taken in conjunction with different saturation values of the work-function change, suggest a different composition and/or structure of the solid solution phases. It appears that the solubility of H in CoTi is lower at 80 than at 300 K. As in $FeTiH_x$ occupation of octahedral sites is expected in α-$CoTiH_x$. The local distortion of the lattice and the site distribution, however, may depend on stoichiometry and temperature. The H-induced electronic states as probed in UPS show, in addition to the quantitative changes, shifts to higher binding energy in the bonding bands on going from low to high H_2 exposures (see Fig. 4). H-bonding levels have been calculated[27] to increase in binding energy with increasing H concentration, and the shifts observed here may be manifestations of this effect.

Another question of interest concerns the location of H in the chemisorbed phase, i.e., does the H go into sites on top of the surface layer or into subsurface sites? Subsurface site occupation of chemisorbed H has recently been demonstrated on Nb surfaces.[28] The UPS, EELS, and TDS results of this study are compatible with either location on CoTi, but the initial increase of the work function favors sites above the surface plane in the chemisorbed phase. The transition from the chemisorbed phase to the solid solution phase appears to be continuous.

The apparent differences in reactivity between the annealed and the unannealed surfaces may have been due to the slightly different surface compositions between the two conditions, but are much more likely to have been due to the greater reactivity known to be characteristic of disordered surfaces. Neither the different [Co]/[Ti] ratios nor the amount of oxygen present are considered to have been of sufficient significance to account for the change in reactivity on annealing. If it is assumed that the excess Co before annealing, and the excess Ti after annealing, were confined to monolayer thickness, then it can be calculated that their fractional coverage of the surface was only about 0.08 in each case. Again, as pointed out earlier, oxygen will have arrived at the surface by means of diffusion from the bulk, and if it is then assumed that the oxygen distribution with depth was uniform, only about one-quarter of the oxygen Auger signal would have arisen from oxygen at the external surface. Thus the actual fractions of Co (Ti) and oxygen residing on the external surface were not large enough to have played any significant role. In addition, Pick *et al.*[26] noted that small amounts of adsorbed oxygen did not act as an effective barrier to the uptake of hydrogen by niobium and tantalum.

The increased reactivity of surfaces following low-energy, low dose, ion bombardment very similar to the conditions used here has been reviewed by Miranda and Rojo.[29] Although the examples quoted by them concern the adsorption only of oxygen-containing molecules, with no mention of hydrogen, the reasons put forward for the effect of the bombardment on the reactivity, in terms of the creation of additional sites associated with point defects and defect clusters, are likely to apply equally to hydrogen adsorption. It is suggested, therefore, that the most likely reason for the observed, although unquantified, additional reactivity towards hydrogen of the unannealed over the annealed surface is due simply to the creation of additional adsorption sites via bombardment-induced disorder.

V. CONCLUSIONS

Hydrogen and deuterium are found to react readily with clean, polycrystalline CoTi surfaces at both 300 and 80 K. H-(D-) induced electronic states have been detected by UPS at 1.5–2 eV and in the region 4–9 eV below E_F. These states have been rationalized by comparison with calculations on FeTiH_x. Accordingly, the 4–9-eV UPS structures have been associated with H- (D-) derived "bonding bands" below the metal *d* bands, and the feature at 1.5–2 eV with metal states transferred from above to below the Fermi level by the metal-hydrogen interaction. EELS had demonstrated the presence of H (D) at or near the surface by the quenching of a surface loss feature, but has provided no evidence for the formation of a surface hydride phase. The Co-Ti stoichiometry of the surface was unaltered by H_2 or D_2 interaction, as shown by AES, indicating the absence of H- (D-) induced surface segregation effects. TDS showed H_2 (D_2) evolution from the sample above 500 K, and desorption behavior supported the formation of a solid solution phase. The work function of sputtered, clean, CoTi surfaces was measured as 3.9±0.025 eV, and the work function increased upon H_2 (D_2) exposure. The results of the present investigation are consistent with H (D) chemisorption followed by the formation of a solid solution α phase with a different composition and/or structure at 300 and at 80 K. A CoTi surface hydride phase was not detected under conditions typical for UHV experiments in accord with thermodynamic constraints.

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