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Summary Abstract: Formation of Cr_2N overlayers on a Fe/Cr{110} crystal

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In this communication we summarize our experiments related to the formation of chromium surface nitride layers on a $Fe_{72}Cr_{28}\{110\}$ surface. These surface nitrides were produced by (i) exposure to molecular nitrogen, (ii) exposure to ammonia, and (iii) segregation of nitrogen to the crystal surface. It was found in all cases that the nitrogen concentration in the selvedge scales linearly with the chromium concentration and that chromium segregation is the rate determining step for the formation of a surface nitride.

The dissociative adsorption of molecular nitrogen on Cr{110} and FeCr(110) surfaces of varying surface composition has been described previously.[1] By comparing the nitrogen dissociation probability on Fe/Cr surfaces of varying compositions prepared by different sputtering/annealing procedures, it was found that small concentrations of iron at the surface have a drastic effect on the activity of chromium with respect to N_2 dissociation. Since geometrical arguments considering the distribution of chromium clusters of sufficient size to dissociate N_2 cannot explain the decrease in dissociation probability, it was concluded that the presence of iron alters the activity of chromium in a subtle way, probably through electronic effects.

In the following we address the segregation of chromium during nitrogen and ammonia exposure to the crystal and compare these results with chromium segregation following nitrogen segregation from the bulk of the crystal. It should be noted that all experiments described here were performed on surfaces contaminated in the 5%–10% range by oxygen and carbon. We were unable to produce an atomically clean alloy surface during the 12-month period of these measurements.

On iron-rich surfaces (i.e., having the bulk composition of the crystal $Fe_{72}Cr_{28}$) it was found that at $T < 550$ K saturation with atomic nitrogen is obtained after a N_2 exposure of

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$\sim 10^6$ L. However, at $T > 550$ K a continuous increase of nitrogen coverage is paralleled by chromium segregation from the bulk of the crystal, eventually leading to the formation of a Cr_2N surface nitride layer.[1] The surface enrichment of chromium by segregation thus leads to additional nitrogen dissociation, and chromium segregation rather than nitrogen dissociation itself must be the rate determining step in the formation of the chromium surface nitride. The structure of the chromium nitride phase has been reported in Ref. 1.

The same conclusions were derived by experiments using NH_3 as a nitriding agent. As with N_2, it was found that NH_3 dissociation to atomic nitrogen depends on the chromium concentration of the surface. The ratios for dissociative adsorption of NH_3 to atomic nitrogen (which was the reaction product monitored by Auger electron spectroscopy) on Cr{110}, $Fe_{72}Cr_{28}(110)$ with a surface concentration of chromium at 65%, and polycrystalline iron[2] is $1{:}0.3{:}10^{-2}$, respectively. As with our results on N_2 dissociation at temperatures below 550 K, the surface was saturated with atomic nitrogen, and chromium segregation was too slow to be detected over reasonable time periods (~ 10 min). At $T > 550$ K, however, chromium segregation to the surface was observed leading to an increase in atomic nitrogen produced by NH_3 exposure.

The third method of producing a chromium nitride surface was by nitrogen diffusion from the bulk. The Fe/Cr alloys were saturated with nitrogen by extensive N_2 exposures and subsequently sputtered at room temperature resulting in a nitrogen-free surface close to the bulk composition $Fe_{72}Cr_{28}$. The crystal was then heated and nitrogen started to segregate to the surface. No change in Fe/Cr surface composition was detectable below 550 K. At temperatures of 645 and 785 K, however, chromium segregated to the surface, as was found in the N_2 and NH_3 experiments. A short delay between nitrogen diffusion and chromium segregation was observed. As with gas exposure, formation of the surface nitride low-energy electron diffraction (LEED) structure was observed at a relative nitrogen coverage of $\Theta = 0.7$.

The relationship between relative nitrogen coverage and chromium enrichment obtained from the segregation and NH_3 exposure experiments are shown in Fig. 1. In both cases the relative nitrogen coverage scales linearly with chromium segregation, although the rates for N segregation and NH_3 dissociation differ by orders of magnitude, emphasizing that chromium segregation to the surface determines the rate of surface nitride formation.

At this point, we have not measured carefully enough the *rate* of chromium segregation as a function of nitrogen coverage for the gas phase exposure methods used to produce a nitride layer. Only for the segregation experiments have the rates been determined to obtain the activation energies for nitrogen segregation in the Fe/Cr alloy. The activation energy for nitrogen segregation in the Fe/Cr alloy was determined to be 57 ± 10 kJ/mol for $\Theta_N \to 0$. This value is slightly lower than the activation energies reported for nitrogen diffusion in α-Fe which range between 68 and 77 kJ/mol.[3-6] The activation energy for chromium segregation to the surface in our experiments was found to be 97 ± 15 kJ/mol. This value is considerably smaller than the activation energy for self-diffusion of chromium in α-iron of 240 kJ/mol.[7] Unfortunately, data for the diffusion of chromium on a clean Fe/Cr alloy surface are not available, because of the severe problems in completely suppressing bulk diffusion of nitrogen and other impurities (O,C) and maintaining a clean surface even in ultrahigh vacuum for a sufficiently long time period. An explanation for the low value of the activation energy of segregation is therefore not possible due to the unknown segregation behavior for an atomically clean surface.

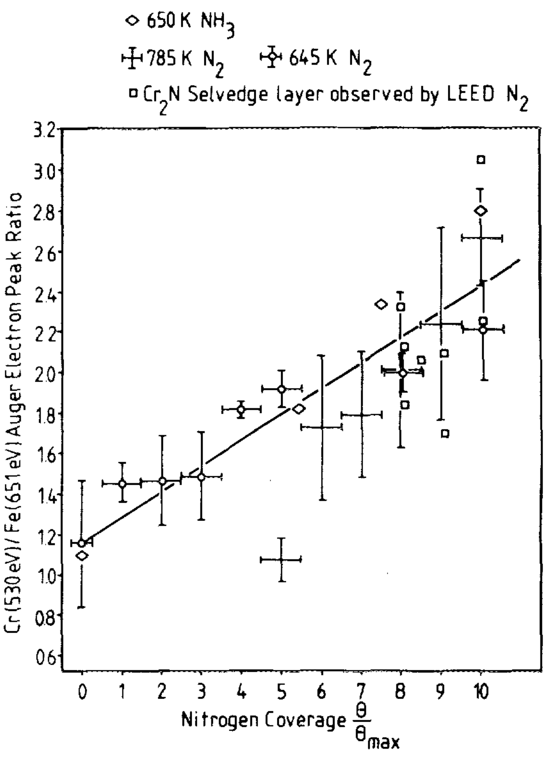

FIG. 1. The relation between chromium enrichment on a $Fe_{72}Cr_{28}$\{110\} crystal surface and relative nitrogen coverage for segregation of nitrogen from the bulk and ammonia decomposition. Substrate temperature: 785, 645, and 650 K, Cr_2N surface nitride observed by LEED.

The main conclusion of this work is that independent of the method by which atomic nitrogen is produced on a Fe/Cr alloy surface, the rate of surface nitride formation is determined by segregation of chromium from the bulk and therefore depends on the sample temperature only. The initial excess in nitrogen concentration on the surface produced by NH_3 exposure does not lead to a different segregation behavior of chromium within the accuracy of our experiments.

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