Part I

Alloying and Effects of Impurities

COSEGREGATION-INDUCED EPITAXIAL GROWTH OF TWO- AND THREE-DIMENSIONAL COMPOUNDS ON MULTICOMPONENT ALLOY SURFACES

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ABSTRACT

In this contribution the cosegregation-induced epitaxial growth of two- and three-dimensional chromium nitrides on ferritic Fe-15%Cr-N(100) ($c_N = 30$ wt-ppm) single crystal surfaces will be discussed. The two-dimensional CrN surface compound is stable between 600 and 720°C. From the (1×1) LEED pattern it is inferred that the surface compound is epitaxial to the bcc(100) alloy surface. XPD and LEED-*IV* investigations have revealed that this surface compound consists of a single CrN compound layer plus an additional subsurface chromium layer with a huge interlayer expansion between both layers. The CrN surface precipitate formed at temperatures $T < 600°$C is also epitaxially arranged on the bcc(100) substrate surface. Its structure corresponds to the rocksalt structure, i.e. the structure of the well-known bulk CrN. Starting from a sputter cleaned alloy surface the growth of the epitaxial CrN surface precipitate proceeds via the two-dimensional CrN surface nitride. After completion of this two-dimensional CrN layer the nucleation and growth of the three-dimensional CrN surface precipitate takes place.

INTRODUCTION

Many chemical and physical properties of materials in high-technology applications depend to a large extent on composition and structure of its external surfaces. Solid surfaces control or at least influence the oxidation/corrosion resistance of materials, their catalytic activity and their magnetic/electronic properties as well. Although this list is by far not complete, it already demonstrates that a deep understanding of surfaces and surface-modification techniques is required if one wishes to modify or even to engineer material properties [1].

In this contribution we will discuss the cosegregation-induced epitaxial growth of two-dimensional surface compounds and three-dimensional surface precipitates on multicomponent alloy surfaces. Cosegregation denotes the joint enrichment of different solute atoms from the bulk of a condensed phase at interfaces. This process may cause the formation of two-dimensional chemical compounds (*surface compounds*). The cosegregation-induced formation of two-dimensional chemical compounds must be distinguished from the precipitation of three-dimensional compounds at surfaces. According to the GIBBS phase rule, three-dimensional precipitates can be formed upon oversaturation in coexistence with the saturated solid solution. Precipitation can take place at free surfaces and grain boundaries where nucleation is favored.

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EPITAXIAL GROWTH OF THE TWO-DIMENSIONAL SURFACE COMPOUND CrN ON Fe-15%Cr-N(100)

The cosegregation-induced formation and the thermal stability of the two-dimensional surface nitride CrN has been investigated on Fe-15%Cr-N(100) alloy surfaces by means of Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and x-ray photoelectron diffraction (XPD). According to chemical bulk analysis, the nitrogen concentration, c_N, in the ferritic single crystal is ≈ 30 wt-ppm.

The temperature dependence of the equilibrium surface coverage is shown in fig. 1. At low temperatures, i.e. $600 \lesssim T \lesssim 680°C$, the corresponding Cr/Fe and N/Fe Auger peak height ratios (PHR) are apparently independent of temperature and correspond to the maximum surface coverages of the segregants. At medium temperatures, i.e. 680 – 780°C, the AES PHR decrease monotonically and are very sensitive to even small temperature changes. At temperatures in excess of 780°C, the surface compositions approach bulk composition of the corresponding alloys.

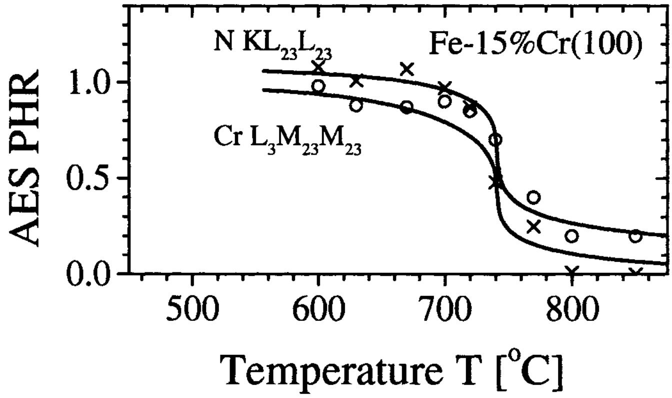

FIGURE 1: Temperature dependence of characteristic Auger PHR $Cr(L_3M_{23}M_{23})/Fe(L_3M_{23}V)$ and $N(KL_{23}L_{23})/Fe(L_3M_{23}V)$ for Fe-15%Cr-N(100) (c_N = 30 wt-ppm). The measurements were performed at a primary energy $E_{kin} = 2$ keV (modulation voltage $V_{PP} = 5$ V). Experimental results are represented by symbols. The solid lines correspond to least square fits between the experimental data and the Guttmann cosegregation model [2].

The experimentally determined AES PHR of the segregants are evaluated according to the Guttmann cosegregation model [2–7]. The corresponding Gibbs free energies of segregation of the metallic and nonmetallic solutes are $\Delta G^o_N = -64$ kJ mole^{-1} and $\Delta G^o_{Cr} = -18$ kJ mole^{-1}, respectively. The interaction energy β is determined as $\beta = -34$ kJ mole^{-1}.

The Fe-15%Cr-N(100) alloy surface exhibits a sharp (1 × 1) LEED pattern after formation of the two-dimensional CrN surface compound (fig. 2) indicating the epitaxial arrangement of this surface compound on the bcc(100) substrate surface. Similar (1 × 1) LEED patterns have also been seen for VC, V(C,N) and TiC surface compounds on ferritic Fe-3%V-C(100), Fe-3%Si-0.04%V-C(100), Fe-3%V-C,N(100) and Fe-6%Al-0.5%Ti-C(100) alloy surfaces [8–11] indicating that all these surface compounds are structurally related.

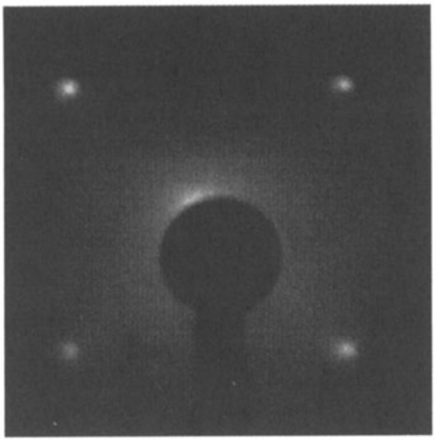

FIGURE 2: LEED pattern of the Fe-15%Cr-N(100) alloy surface after formation of the two-dimensional CrN surface compound at 620°C ($E_p = 50$ eV).

Recently a (1×1) LEED pattern has also been obtained for a WN surface compound formed via cosegregation of tungsten and nitrogen on an Fe-9%W-N(100) alloy surface [12].

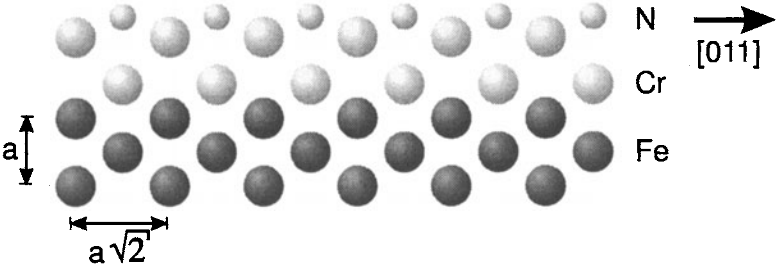

FIGURE 3: Structure model for the segregated CrN surface compound on Fe-15%Cr-N(100). The surface compound consists of two layers of Cr atoms (light grey) and N atoms at the surface. Shown is a vertical cut through the crystal along the $[011]_{\mathrm{bcc}}$ azimuthal direction.

The most probable structural relationship between (1×1) CrN surface compound and bcc(100) substrate surface can be derived from the (100) plane of the rocksalt structure, i.e. the structure of the three-dimensional chromium nitride CrN that exists in the phase diagram of the Cr-N and Fe-Cr-N systems. The epitaxial relationship is given by

$$\begin{array}{ccc} (100)_{\mathrm{bcc}} & \| & (100)_{\mathrm{CrN}} \\ [001]_{\mathrm{bcc}} & \| & [011]_{\mathrm{CrN}}\,. \end{array} \tag{1}$$

A first structural analysis of the two-dimensional CrN surface compound has been performed using XPD [13–15]. It has been found that the CrN surface compound consists

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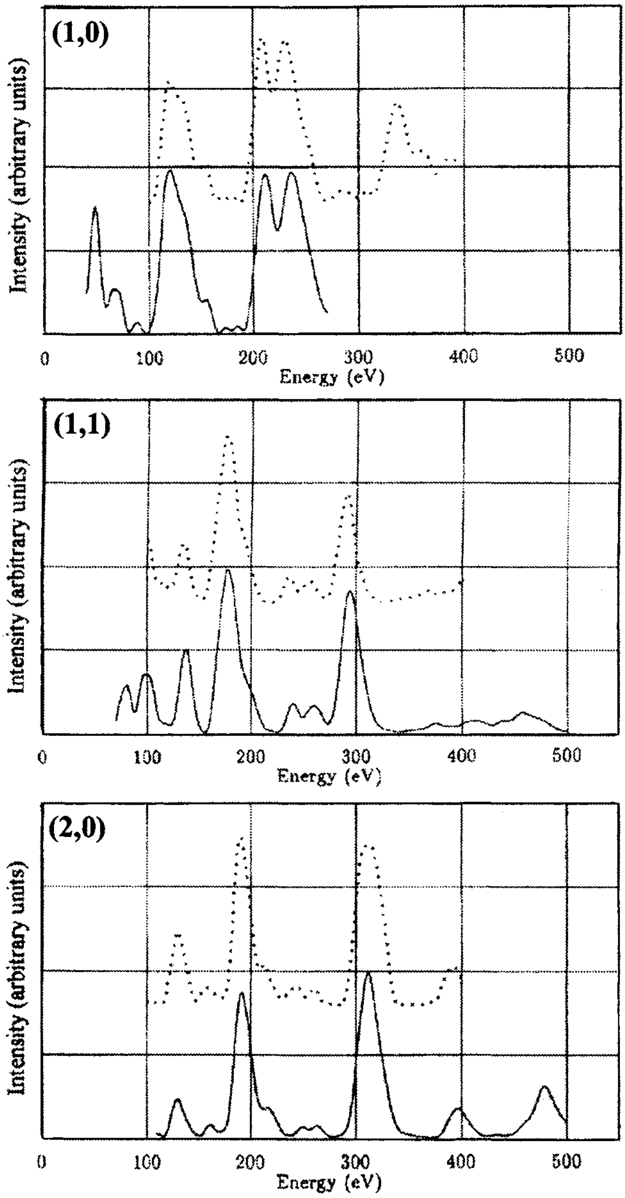

FIGURE 4: Comparison of experimental and best fit spectra for a selection of beams for the two-dimensional CrN surface compound.

of two Cr layers epitaxially arranged on the bcc(100) surface with a single N layer arranged slightly above the outermost M layer (fig. 3).

In order to clarify structural details of the CrN surface compound we have performed a detailed investigation based on low energy electron diffraction (LEED-IV). Full details of the analysis are given in [16] and will not be repeated here. The measured LEED spectra (fig. 4) were analyzed by conventional full dynamical programs [17] combined with *Tensor LEED* [18,19], *Chemical Tensor LEED* [20–23] and *Thermal Tensor LEED* [20,23,24]. The directed automatic structural search procedure was guided by the Pendry R-factor [25]. The agreement between experimental and best fit spectra is excellent (fig. 4).

The best fit (Pendry R-factor $R = 0.14$, $var(R) = 0.024$) is achieved for a full nitrogen layer ($c_N = 100\%$) with nitrogen atoms residing in hollow sites at a height of $d_{01} = 0.09 \pm 0.03$ Å above the outermost metal layer. The distances between the metal layers result to $d_{12} = 1.82 \pm 0.02$ Å, $d_{23} = 1.39 \pm 0.02$ Å, $d_{34} = 1.46 \pm 0.02$ Å. Compared to the bulk value, $d_0 = 1.43$ Å, this corresponds to a huge expansion of the interlayer distance between the segregated Cr layers $\Delta d_{12}/d_0 = +27 \pm 2$ % while the relaxation values of deeper layer distances are in the usual range found at surfaces ($\Delta d_{23}/d_0 = -3 \pm 2$ %, $\Delta d_{34}/d_0 = +2 \pm 2$ %).

It is quite interesting to note that the Cr→Cr interlayer distance is expanded by about 27% with respect to the ideal bcc spacing. The nitrogen atoms are arranged in the fourfold hollow positions slightly above the outermost Cr layer. Very similar interlayer expansions have been found also in the course of a LEED study of nitrogen segregated on a Cr(100) single crystal surface [26,27]. These authors have found an expansion of the Cr lattice of 23-25% between first and second layer and the N atoms located in fourfold hollow sites. In Ref. [15] these huge interlayer expansions are interpreted as indicative of a structural transformation towards a CrN surface compound of rocksalt structure where the interlayer expansion is 41% relative to bcc bulk Fe-Cr-N alloy.

EPITAXIAL GROWTH OF THE THREE-DIMENSIONAL SURFACE PRECIPITATE CrN ON Fe-15%Cr-N(100)

According to the phase diagram of the ternary system Fe-Cr-N, the precipitation of the three-dimensional bulk chromium nitride CrN is possible in Fe-15%Cr-30ppmN specimen below a transition temperature of $T_T^{bulk} \approx 600°$C. However, the precipitation of CrN may also occur at surfaces and is discussed in detail below.

In fig. 5 the segregation kinetics of sputter cleaned Fe-15%Cr-N(100) single crystals with a nitrogen content of 30 wt-ppm is shown for two representative temperatures. At temperatures well above T_T^{bulk} (fig. 5a) the characteristic Cr($L_3M_{23}M_{23}$)/Fe(L_3M_{23}V) and N($KL_{23}L_{23}$)/Fe(L_3M_{23}V) Auger PHR are independent of time after the desired temperature is established. The cosegregation-induced formation of the two-dimensional CrN surface compound is obviously very fast compared to the annealing procedure. At temperatures well below T_T^{bulk} (fig. 5b) the cosegregation takes a substantially longer time as the bulk diffusion of the segregants is slowed down. After about 20h the segregation kinetics exhibit a wide plateau which is attributed to the formation of an intermediate two-dimensional CrN surface compound. Further growth of the nitride leads to three-dimensional CrN surface precipitates. It is probably important to recall that the CrN surface precipitation is caused by a substantial nitrogen oversaturation of the ferritic bulk. Thus, surface precipitation is a continuous process which may stop if most of the bulk

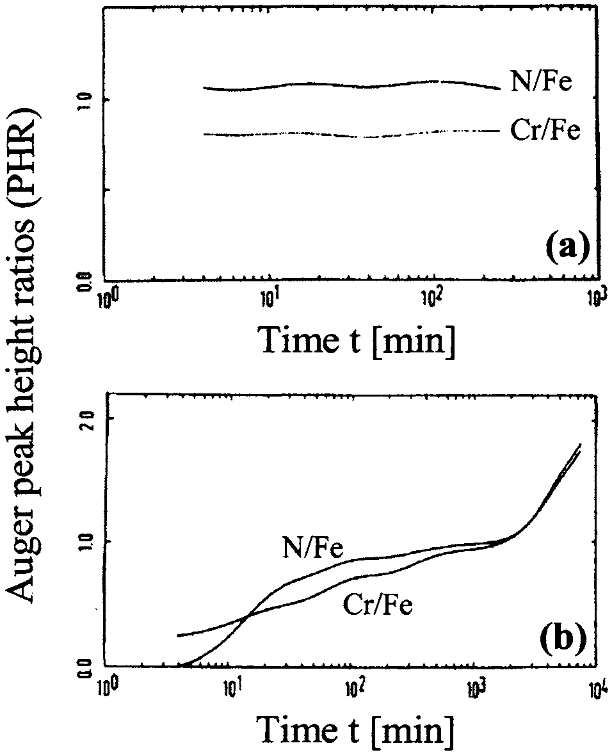

FIGURE 5: Segregation kinetics of Fe-15%Cr-N(100) single crystals after sputter cleaning and annealing to 630°C (a) and 490°C (b), respectively. $Cr(L_3M_{23}M_{23})/Fe(L_3M_{23}V)$ and $N(KL_{23}L_{23})/Fe(L_3M_{23}V)$ Auger peak height ratios are used to characterize the surface composition. The data registration was started when the desired sample temperature was established, i.e. after about 5 min.

nitrogen is precipitated. Therefore, the CrN thickness strongly depends on the duration of the annealing procedure. In some cases we have performed sputter depth profiling to estimate the thickness of the surface precipitate. After ageing for 100 h at 490°C, the thickness of the surface precipitate is about 2-5 nm. LEED investigations still reveal (1×1) pattern (similar to those shown in fig. 2, but with a significantly increased background intensity). Therefore, we conclude (i) that the surface precipitates grow epitaxially on the bcc(100) alloy surface and (ii) that the CrN surface precipitates exhibit the structural relationship given by Eq. 1.

As already mentioned, surface precipitation cannot take place at temperatures above $\approx$ 600°C, i.e. when the solubility limits of the segregants are not exceeded. Thus, at a transition temperature $T_T \approx 600°C$ a phase transition between two-dimensional CrN surface compound and three-dimensional CrN surface precipitation takes place.

CONCLUSIONS

Surface segregation is a very complex but also a very fascinating phenomenon which has attracted considerable attention in the past. In this contribution the focus was on the cosegregation-induced formation of two-dimensional surface compounds and three-dimensional surface precipitates in the system Fe-15%Cr-N(100). At sufficiently high temperatures i.e. when bulk diffusion of the segregants is rapid, surface compound formation is thermodynamically controlled. The CrN surface compound is epitaxially stabilized on the (100) surface of the bcc alloy. Structural details are obtained by XPD and LEED. The growth of epitaxially arranged three-dimensional surface precipitates can occur when the solubility limits of the segregants are exceeded, i.e. below ≈ 600°C in the Fe-15%Cr-N system with $c_N \approx 30$ wt-ppm. The CrN surface precipitate is found to grow epitaxially on (100) oriented substrate surfaces. The two-dimensional CrN surface compound is formed as an intermediate surface phase during the initial nucleation step of the precipitation process.

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REFERENCES

1. C. Uebing, Heterogeneous Chemistry Reviews **3**, 351 (1996).
2. M. Guttmann and D. McLean in Interfacial Segregation, edited by W.C. Johnson and J.M. Blakely (American Society for Metals, Metals Park, 1977).
3. M. Guttmann, Metall. Trans. A **8**, 1383 (1977).
4. M. Guttmann, Surf. Sci. **53**, 213 (1975).
5. M. Guttmann, P.R. Krahe, F. Abel, G. Amsel, M. Bruneaux, and C. Cohen, Metall. Trans. **5**, 167 (1974).
6. P. Dumoulin and M. Guttmann, Mater. Sci. Eng. **42**, 249 (1980).
7. M. Guttmann, Mater. Sci. Eng. **42**, 277 (1980).
8. H. Viefhaus, J. Peters, and H.J. Grabke, Surf. Interface Anal. **10**, 280 (1987).
9. C. Uebing and H. Viefhaus, Surf. Sci. **236**, 29 (1990).
10. C. Uebing, H. Viefhaus, and H.J. Grabke, Surf. Sci. **264**, 114 (1992).
11. C. Uebing, Ber. Bunsenges. Phys. Chem. **99**, 951 (1995).
12. V. Hille, E.C. Viljoen, and C. Uebing, Surf. Sci. Lett. **367**, L54 (1996).
13. C. Uebing, V. Scheuch, M. Kiskinova, and H.P. Bonzel, Surf. Sci **321**, 89 (1994).

14. C. Uebing, V. Scheuch, M. Kiskinova, and H.P. Bonzel, Surface Reviews and Letters **3**, 1721 (1996).

15. V. Scheuch, M. Kiskinova, H.P. Bonzel, and C. Uebing, Phys. Rev. B **51**, 1973 (1995).

16. Ch. Müller, C. Uebing, M. Kottcke, Ch. Rath, L. Hammer, and K. Heinz Surf. Sci., in print.

17. M.A. Van Hove and S.Y. Tong, Surface Crystallography by LEED, (Springer, Berlin, 1979).

18. P.J. Rous, J.B. Pendry, D.K. Saldin, K. Heinz, K. Müller and N. Bickel, Phys. Rev. Lett. **57**, 2951 (1986)

19. P.J. Rous, Progr. Surf. Sci. **39**, 3 (1992)

20. K. Heinz, Rep. Progr. Phys. **58**, 637 (1995)

21. R. Döll, M. Kottcke and K. Heinz, Phys. Rev. B **48**, 1973 (1993)

22. K. Heinz, M. Kottcke, U. Löffler and R. Döll, Surf. Sci. **357-358**, 1 (1996)

23. K. Heinz, R. Döll and M. Kottcke, Surf. Rev. & Lett. **3**, 1651 (1996)

24. U. Löffler, R. Döll, K. Heinz and J.B. Pendry, Surf. Sci. **301**, 346 (1994)

25. M. Kottcke and K. Heinz, Surf. Sci. **376**, 352 (1997)

26. Y. Joly, Y. Gauthier, and R. Baudoing, Phys. Rev. B **40**, 10119 (1989).

27. F. Scheurer, P. Ohresser, B. Carrière, J.P. Deville, R. Baudoing-Savois, and Y. Gauthier, Surf. Sci. **298**, 107 (1993).