

Formation of Ultrathin Ordered Surface Phases by Segregation

Burkhard Eltester, Elmarie C. Viljoen and Christian Uebing
Max-Planck-Institut für Eisenforschung

D-40237 Düsseldorf, Germany

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Abstract

In this contribution experimental surface segregation studies of nonmetallic solutes on metals and alloys will be reviewed. The focus will be on recent studies of cosegregation phenomena on multicomponent alloy systems. In recent years many efforts have been undertaken to establish a detailed understanding of such processes. It is now generally accepted that cosegregation may cause the formation of two-dimensional chemical compounds (surface compounds), which are representatives of a new class of chemical compounds in two dimensions. In many cases surface compounds are epitaxially stabilized on the corresponding substrate surface.

1. Introduction

Many chemical and physical properties of materials in high-technology applications depend to a large extent on composition and structure of their 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].

Despite their enormous technological importance, our basic understanding of simplest metal and alloy surfaces is not well developed. It is increasingly recognized, however, that truly technological advances may result from a better comprehension and control of surface phenomena. The controlled adsorption and segregation of nonmetals such as carbon, nitrogen and oxygen on solid surfaces are probably the most simplest techniques for the surface-modification of metals and alloys. These processes frequently result in the formation of ultrathin two-dimensional transition metal compounds, such as carbides, nitrides and oxides. In many cases these compounds are well ordered and epitaxially stabilized on surfaces of suitable orientation and structure.

In recent years there has been a substantial progress especially on the cosegregation-induced formation of two-dimensional carbides and nitrides on alloy surfaces. Most of

the alloy systems investigated so far are body-centered cubic (bcc) and can be considered as model systems for commercial steels. Although it is now generally accepted that two-dimensional compounds can change the properties of alloy surfaces, the underlying atomistic mechanisms are still unclear. Only in some exceptional cases two-dimensional surface compounds seem to induce a significant improvement of distinct surface properties. For instance, early studies on the cosegregation-induced formation of a two-dimensional titanium carbide TiC on an Fe-6%Al-0.5%Ti-C(100) alloy indicate that the two-dimensional TiC can significantly enhance the adherence of aluminium oxide layers in oxidizing atmospheres especially in case of thermal cycling [2].

In this contribution we will discuss the segregation-induced formation of ultrathin ordered surface phases. The emphasis will be on recent studies of cosegregation phenomena on multicomponent alloy systems. During the last few years many efforts have been undertaken to establish a detailed understanding of such processes. Cosegregation may cause the formation of two-dimensional ordered chemical compounds (**surface compounds**) which are representatives of a new class of low dimensional chemical compounds. In many cases surface compounds are epitaxially stabilized on the corresponding substrate surface. Such two-dimensional surface compounds offer access to a broad spectrum of amazing physical phenomena, e.g. two-dimensional conductivity and superconductivity,

two-dimensional magnetism, phase transitions in two dimensions etc.. It is very likely that such surface compounds which are easily prepared in a surface science laboratory may become a promising playground of scientists and engineers of very different disciplines.

2. Surface Segregation of Nonmetallic Solutes on Metals

In the seventies and eighties of the 20th century much attention has been given to experimental investigations of the surface segregation of nonmetallic solutes on metals. Segregation denotes the enrichment of solute atoms from the bulk of a condensed phase at interfaces. Many experimental studies have been devoted to nonmetal segregation on iron surfaces obviously because of the large technological importance of iron and steel. Some of the systems studied in detail have been carbon on α -Fe [3-6], nitrogen on α -Fe [4, 7], oxygen on α -Fe [8, 9], silicon on α -Fe [10-14], phosphorus on α -Fe [15, 16] and sulphur on α -Fe [4, 17]. Moreover, the segregation of carbon to single crystalline Ni surfaces has also been studied in large detail by Blakely and coworkers [18-23].

In this contribution I will not penetrate further into this very interesting field. It is quite obvious that such a task would exceed the scope of the present review. Therefore, the interested reader is referred to several excellent review articles which have been recently published [24].

3. Surface Segregation of Nonmetallic Solutes on Multicomponent Alloys

In ternary or even more complex alloy systems the joint enrichment of two (or more) solutes at surfaces and grain boundaries is possible. During the late seventies of the 20th century studies of these so-called cosegregation phenomena have attracted considerable interest, which basically has been driven by the need to understand the influence of cosegregation processes on the temper embrittlement of steels [25]. The first systematic investigation of such cosegregation phenomena has been performed by DUMOULIN and GUTTMANN using dilute ternary iron-based alloys Fe-M-X with M as metallic solutes (M: Ni, Cr, V, Ti, Mo) and X as metalloid impurities (X: Sb, P, S, C, N) [26]. Their pioneering work demonstrates clearly that cosegregation can be unequivocally attributed to strong attractive interactions

between the metallic and nonmetallic solutes M and X e.g., between Ni-Sb, Ti-Sb, Mo-P, Ti-P, Cr-N, Mo-N, V-N, Mo-C, V-C, Ti-C and Ti-S [26].

The possibility of segregation and cosegregation induced formation of two-dimensional compounds has been discussed in detail at first by GUTTMANN [27]. Almost one decade later VIEFHAUS, PETERS and GRABKE provided the first experimental evidence of a two-dimensional surface compound formed upon cosegregation of the constituent components. These authors studied the surface segregation under UHV conditions as well as the initial stages of growth and composition of protecting oxide- and oxycarbide layers on Fe-6%Al-0.5%Ti-C(100) alloy single crystals [2]. Under UHV conditions a two-dimensional surface compound TiC is formed at elevated temperatures as an interlayer between substrate surface and a segregated $p(1 \times 1)$ Al layer. In oxidizing atmospheres a titanium oxycarbide layer Ti(C,O) is formed which is covered by an epitaxially very dense and well adherent Al_2O_3 layer.

Since then surface compound formation has been studied in detail for a variety of bcc and fcc iron-based alloys. Unfortunately, it is impossible to discuss all these systems in the framework of this contribution and, therefore, we will restrict our considerations to some of the more general aspects of surface compound formation, namely the cosegregation-induced formation of epitaxially stabilized two-dimensional surface nitrides (Sec. 3.1) and the cosegregation-induced morphological instabilities of bcc(110) and bcc(111) alloy surfaces (Sec. 3.2).

3.1 Cosegregation-induced Formation of epitaxially stabilized two-dimensional Surface Nitrides on Transition Metal Alloys

In a recent study the formation and thermal stability of the two-dimensional surface nitrides CrN, MoN and WN on transition metal alloy surfaces has been investigated by means of Auger electron spectroscopy(AES) and low energy electron diffraction (LEED) [28]. The ultrathin surface nitrides are prepared by means of cosegregation of the constituents on Fe-15%Cr-N(100), Fe-3.5%Mo-N(100) and Fe-9%W-N(100) single crystals. In all cases the nitrogen concentrations in the ferritic single crystals have been in the low ppm range,

$c_N < 51$ wt-ppm.

The temperature dependence of the equilibrium surface coverage is shown in Fig. 1 for the three alloys. The general shape of these curves is very similar albeit the curves are significantly shifted with respect to the temperature axis for the different surface nitrides. This effect is most prominent for the WN surface nitride which is formed at temperatures below 600°C only. In contrast, the MoN and CrN surface compounds are thermally much more stable as these compounds are also formed at higher temperatures. At low temperatures, i.e. $T < 520^\circ\text{C}$ (WN), $T < 650^\circ\text{C}$ (MoN) and $T < 680^\circ\text{C}$ (CrN), the corresponding W/Fe, Mo/Fe, Cr/Fe and N/Fe Auger PHR are apparently independent of temperature and correspond to the maximum surface coverages of the segregants. At medium temperatures, i.e. 520-600°C (WN), 650-760°C (MoN) and 680-780°C (CrN), the AES PHR decrease monotonically and are very sensitive to even small temperature changes. At temperatures in excess of 600°C (WN), 760°C (MoN) and 780°C (CrN) the surface compositions approach bulk composition of the corresponding alloys.

The experimentally determined Auger peak height ratios (PHR) of the segregants are evaluated according to the Guttman cosegregation model [25-27, 29-31]. Details of this procedure are given in [28]. The corresponding Gibbs free energies of segregation of the metallic and nonmetallic solutes and the interaction energy β are shown in Table. 1. The ΔG_N^s values are significantly higher for the MoN and CrN surface compounds ($\approx 65 \text{ kJ mol}^{-1}$) than for the WN surface compound (56 kJ mol^{-1}). The same tendency is seen for the interaction energy β albeit at lower values (around 25-35 kJ mol^{-1}). The ΔG_M^s values decrease monotonically from 18 kJ mol^{-1} for the CrN to 11 kJ mol^{-1} for the WN surface compound.

The Fe-15%Cr-N(100), Fe-3.5%Mo-N(100) and Fe-9%W-N(100) surfaces exhibit sharp (1×1) patterns after formation of the CrN,

MoN and WN surface nitrides indicating the epitaxial arrangement of the surface compounds on the corresponding substrate surfaces. Very similar (1×1) 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 [2, 32{34} indicating that all these surface compounds are structurally related.

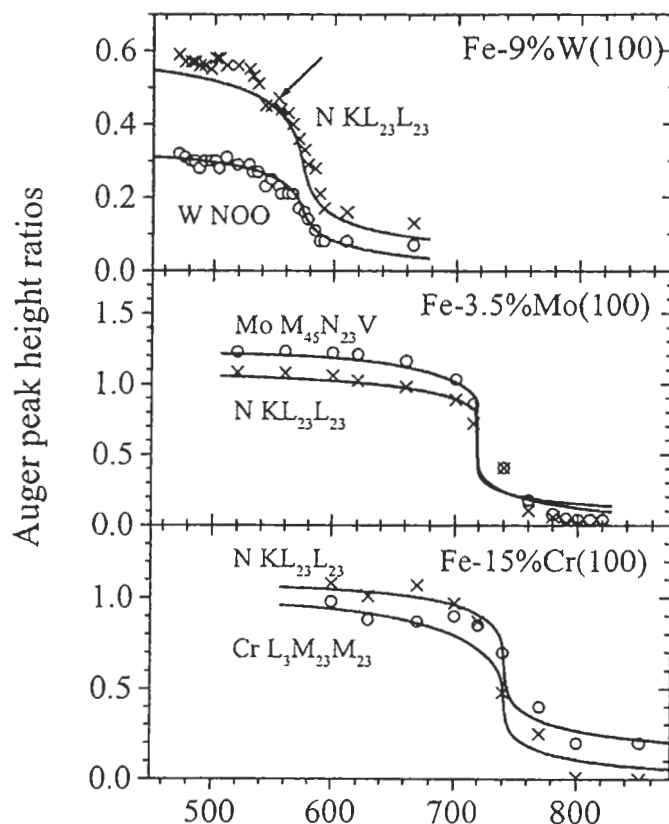


Fig.1 Temperature dependence of Auger PHR W/Fe, Mo/Fe, Cr/Fe and N/Fe for (a) Fe-9%W-N(100) ($c_N = 51$ wt-ppm), (b) Fe-3.5%Mo-N(100) ($c_N = 10$ wt-ppm), and (c) Fe-15%Cr-N(100) ($c_N = 30$ wt-ppm). The measurements were performed at a primary energy $E_{kin} = 2 \text{ keV}$ (modulation voltage $V_{pp} = 5 \text{ V}$). Experimental results are represented by symbols. The solid lines correspond to least square fits between the experimental data and the Guttman cosegregation model [25].

Table 1: Compilation of Gibbs free energies of segregation of the metallic and nonmetallic and interaction energies obtained from Fig. 1 according to the Guttman cosegregation model, after [28].

surface nitride	alloy surface	ΔG_N^s [kJ mol^{-1}]	ΔG_M^s [kJ mol^{-1}]	β [kJ mol^{-1}]
CrN	Fe-15%Cr-N(100)	64	18	34
MoN	Fe-3.5%Mo-N(100)	67	15	35
WN	Fe-9%W-N(100)	56	11	26

The most probable structural relationship between MX surface compound and the bcc(100) substrate surface can be derived from the (100) plane of the rocksalt structure with the epitaxial relationship between given by

$$\begin{aligned} (100)_{\text{bcc}} &\parallel (100)_{\text{MX}} \\ [001]_{\text{bcc}} &\parallel [011]_{\text{MX}} \end{aligned} \quad (1)$$

as is discussed in more detail in [28]. We note that in the binary M–X systems mentioned so far three-dimensional compounds MX with rocksalt structure exist.

Recently structural details of the two-dimensional surface compounds MoN and CrN on Fe-3.5%Mo-N(100) and Fe-15%Cr-N(100) alloy surfaces have been clarified by x-ray photoelectron diffraction (XPD) and low energy electron diffraction (LEED-IV) [35-37]. It has been found that both surface compound consist of two M layers epitaxed on the bcc(100) surface with a single N layer arranged slightly above the topmost M layer (Fig. 2). The nitrogen atoms are arranged in the fourfold hollow positions of the topmost M layer. It is quite interesting to note that the M → M interlayer distance is expanded by about 20% with respect to the ideal bcc spacing. 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 [38, 39]. In these studies an expansion of the Cr lattice of 23-25% between first and second layer and the N atoms located in fourfold hollow sites was found.

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-30 ppmN specimen at temperatures below $\approx 600^\circ\text{C}$. However, the precipitation of CrN may also occur at surfaces and has been investigated in detail on Fe-15%Cr-N(100) single crystals at such low temperatures [40, 41]. The formation of an epitaxially arranged (two-dimensional) CrN surface compound is the initial nucleation step of the precipitation process. Further growth of the nitride leads to surface precipitates, which exhibit the structural relationship given by Eq. 1. At a transition temperature $T_\tau \approx 600^\circ\text{C}$ the reversible transition between three-dimensional CrN surface precipitation and two-dimensional CrN surface compound formation takes place. In [41] this process has been classified as a surface phase transition.

3.2 Cosegregation-induced Morphological Instabilities of (110) and (111) oriented ferritic Alloy Surfaces

Cosegregation-induced morphological instabilities of (110) and (111) oriented surfaces of random mixing body centered cubic alloys have recently been studied applying Auger electron spectroscopy, low energy electron diffraction and scanning electron microscopy [42]. Surface cosegregation has been investigated on (110) and (111) oriented Fe-15%Cr-N, Fe-3%V-C, Fe-3%V-N and Fe-3%V-C,N single crystals. Cosegregation induces the faceting of the bcc(111) and (110) alloy surfaces.

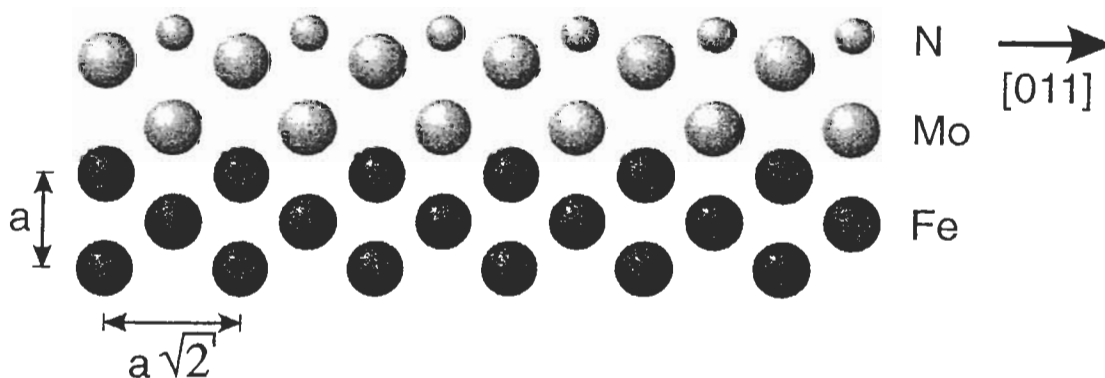


Fig.2 Structure model of the segregated MoN surface compound on Fe-3.5%Mo-N(100). This compound consists of two layers of Mo atoms (light grey) and N atoms at the surface. Shown is a vertical cut through the crystal along the $[011]_{\text{bcc}}$ azimuthal direction, after [35].

3.2.1 BCC(111) Surfaces

Ageing of Fe-15%Cr-N(111) samples with nitrogen contents $c_N > 100\text{ppm}$ at $T \leq 600^\circ\text{C}$ causes surface precipitation of CrN [42, 43]. This process significantly changes the appearance of the previously flat and (on the resolution scale of scanning electron microscop) unstructured clean alloy surface. Upon CrN surface precipitation the originally mirror-like (111) surface becomes irreversibly opaque. Optical and SEM micrographs of such surfaces (Fig. 3) show the existence of small craters typically of about $2\ \mu$ in diameter, which are not visible on aged Fe-15%Cr-N (111) samples with nitrogen contents

$c_N \ll 100\ \text{ppm}$. These micrographs suggest that the Fe-15%Cr-N (111) surface is subject to cosegregation-induced facetting of the bcc(111) surface [42]. Using LEED we have been able to determine the facet orientation as

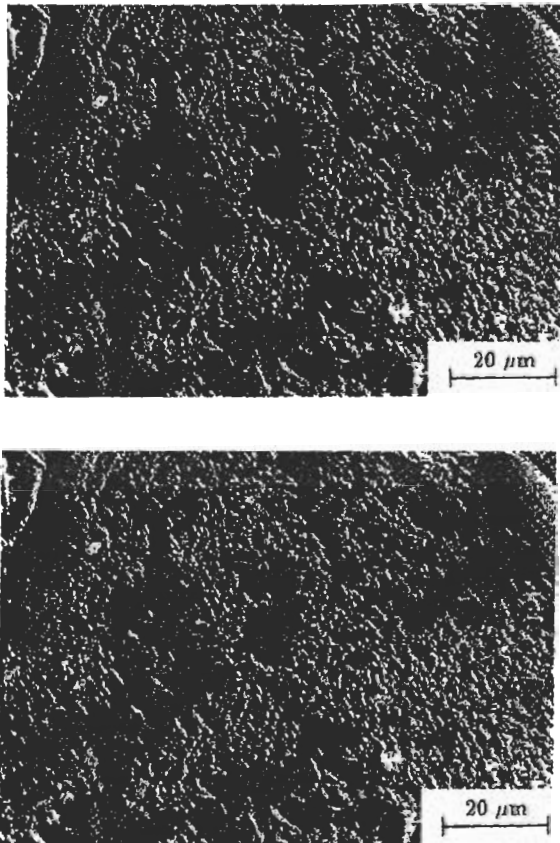


Figure 3: Optical (a) and scanning electron micrographs (b) of Fe-15%Cr-N(111) after ageing for 12 h at 560°C showing the facetting of the bcc(111) surface induced by the cosegregation of chromium and nitrogen, after [42].

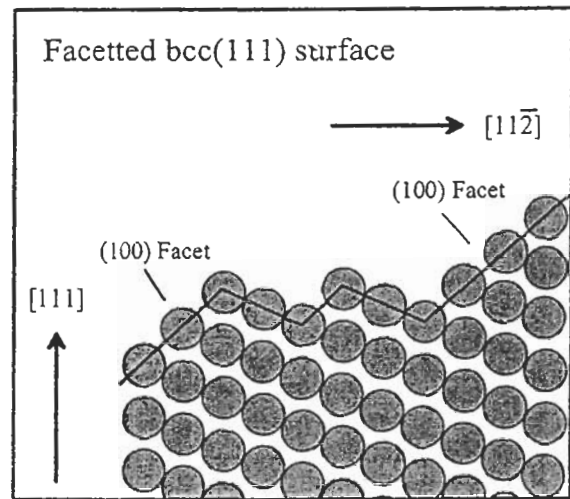


Figure 4: Schematic cross-section showing the faceted bcc(111) surface, after [42]. LEED investigations have revealed the facet orientation to correspond to (100).

{100} (Fig. 4). This result is plausible, since the bcc (100) surface is well suited for the epitaxial stabilization of CrN surface compounds and surface precipitates as well [42].

Cosegregation-induced morphological instabilities have also been observed on ferritic Fe-3%V-C(111) and Fe-3%V-C,N(111) surfaces which at elevated temperatures exhibit the formation of two-dimensional VC, VN and V(C,N) surface compounds [43]. Again scanning electron microscopy shows the existence of macroscopic facets on such surfaces being separated by apparently at areas in between [43]. Therefore, it can be concluded that the observed facetting of the (111) oriented surfaces studied in the present work points to the general phenomenon of cosegregation-induced morphological instability of bcc alloy surfaces.

We conclude this section by noting that morphological instabilities are frequently observed in case of metal films evaporated on bcc surfaces. Some of the most recent studies by Madey et.al. have focused on atomically rough bcc(111) surfaces [44 – 49]. These studies have revealed a striking morphological instability of annealed W(111) and Mo(111) surfaces covered with several transition and noble metals, e.g. Pt, Pd, Au, Rh and Ir.

3.2.2 BCC(110) Surfaces

Cosegregation-induced morphological instabilities have also been observed on

bcc(110) alloy surfaces. Again cosegregation leads to the formation of two-dimensional isomorphic CrN, VC, VN and V(C,N) surface compounds [42]. After equilibration and annihilation of surface defects the (110) substrate surfaces under investigation exhibit (4×1) LEED patterns with sharp, discrete spots at a low background intensity. In order to rationalize the observed (4×1) LEED patterns a missing and added row model for the cosegregation-induced reconstruction of the bcc(110) surface has been proposed [42].

4 Conclusions

In this contribution the segregation-induced formation of ultrathin ordered surface phases on multicomponent alloys has been described. In such alloys striking cosegregation phenomena may arise, for instance the formation of two-dimensional surface compounds on corresponding substrate surfaces. Surface compounds may be stabilized by epitaxy on surfaces of suitable structure, e.g. CrN, MoN and WN on bcc(100) surfaces. If epitaxial stabilization is not possible, e.g. on bcc(110) and (111) surfaces, very interesting structural reconstructions and facettings can occur, pointing to the morphological instability of such alloy surfaces.

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