

Competition of arsenic and sulfur segregation on Fe-9%W(100) single crystal surfaces

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High-resolution medium-energy ion scattering (MEIS) was used to investigate the segregation of arsenic and sulfur on the (100) oriented surface of a body-centered cubic Fe-9 wt % W(100) single crystal containing 53 wt-ppm As and 10 wt-ppm S. At temperatures ranging from 800 to 1100 °C, both segregants compete for the available surface sites. Arsenic segregation dominates at temperatures around 800 °C where maximum As surface concentrations of $\theta_{\text{As}}^{\text{max}}=0.40$ were found. S segregation is most pronounced at temperatures around 1000 °C with $\theta_{\text{S}}^{\text{max}}=0.43$. MEIS shows the segregated As (S) atoms to be arranged 1.27 Å (1.22 Å) above the topmost metal layer. The metal-to-metal layer distances show an oscillatory behavior with an expansion of the first to second metal layer (+0.05 Å). With As and S on the surface, there is a strong W depletion of the topmost three metal layers. © 1999 American Institute of Physics. [S0003-6951(99)01023-2]

Many chemical and physical properties of materials in high-technology applications, such as their oxidation/corrosion resistance, their catalytic activity and their magnetic/electronic properties, depend on the composition and structure of their external surfaces. A detailed understanding of surfaces and surface modification techniques is required if one wishes to modify or engineer these properties.¹ The controlled segregation of bulk dissolved elements to solid surfaces is probably the simplest technique for surface modification of metals and alloys. Segregation denotes the enrichment of solute or solvent atoms from the bulk of a condensed phase to interfaces. This process may cause the formation of ordered surface phases. In general, segregation processes require bulk diffusion of the segregants and, therefore, segregation plays a role at elevated temperatures only.

In ternary or more complex alloy systems the joint enrichment of two (or more) species is possible. These cosegregation processes may result in the formation of two-dimensional surface compounds on alloy surfaces, as reviewed recently.² In all these studies, however, only highly idealized alloy substrates, grown from repeatedly zone-melted pure elements, have been used. Alloys used for practical applications are usually produced in large quantities and contain many different chemical elements, most of them as traces. The most prominent impurities are the so-called tramp elements, e.g., S, P, Sb, Sn, and As. Tramp elements are present in commercial steels at least in the 10-100 wt-ppm range, and due to the increasing use of low quality scrap in steel production, the content of tramp elements in steels is likely to rise in the near future.

Major changes in properties of steels are caused by the surface or grain-boundary segregation of tramp elements.

Many early studies on segregation phenomena in steels were aimed at elucidating temper embrittlement caused by the grain-boundary segregation of tramp elements.³⁻⁵ The segregation of As has been studied by Costa, Carraretto, Godowski, and Marcus in a combined Auger-electron spectroscopy (AES)/x-ray photoelectron spectroscopy (XPS) analysis using polycrystalline Fe samples containing ≈ 300 wt-ppm As, ≈ 90 wt-ppm P, and ≈ 15 wt-ppm S.^{6,7} As, P, and S compete for the available surface sites. The maximum surface coverage of As was $\theta_{\text{As}}=0.33\pm 0.02$,⁷ found at 760 °C. At $T=800$ °C As does not segregate anymore and the Fe surface is saturated with S only. It is important to note that the low yields of the As MVV and As LMM Auger transitions at 31 and 1228 eV result in small As AES peaks, which do not permit a quantitative analysis. Godowski *et al.* estimated the As Auger detection limit as ≈ 0.30 of a monolayer (ML).⁷ Since AES is routinely used to detect surface contaminants, it is conceivable that As is frequently overlooked on alloy and steel surfaces.

No information is available for As segregation on structurally well-defined surfaces of iron or iron-based alloys. Pure iron single crystals are difficult to grow, and thus we used an Fe-9 wt % W alloy where stable single crystals are accessible. In this letter we focus on the segregation of the tramp elements As and S on a Fe-9 wt % W(100) single crystal. The crystal was grown via the vertical Bridgman technique from a cylindrically shaped Fe-9%W premelt ($\phi = 20$ mm) using zone melted iron as base material. This procedure usually yields alloy crystals of high quality and purity. The typical impurity concentrations of the unavoidable nonmetals C, N, O, and S are in the 10 wt-ppm range. In the present case we accidentally reused a contaminated quartz tube for the preparation of the premelt, and this caused substantial uptakes of As, Nb, and Sn into the premelt and also into the final crystal. Chemical analysis showed the principal contaminants to be As (53 wt-ppm), Nb (23 wt-ppm), Sn (54

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wt-ppm), and S (10 wt-ppm). Thus this crystal is almost ideally suited to systematically investigate the segregation of tramp elements on a structurally well defined alloy substrate.

Crystals were cut into slices of $5 \times 5 \times 1.5 \text{ mm}^3$ by spark erosion, and then were ground and polished mechanically. After introduction into the ultrahigh vacuum (UHV) system, the samples were cleaned by sputtering and heating cycles. The complex segregation behavior of contaminated (100) oriented Fe-9%W single crystals was studied using medium-energy ion scattering (MEIS).

MEIS⁸ is a high energy resolution version of Rutherford backscattering spectroscopy used in the channeling and blocking configuration. A collimated monoenergetic beam of ions (typically H^+ or He^+ with an energy in the range 50–200 keV) is directed at a crystalline target along a direction of high symmetry. Deflection of the ions from the first atom along a row parallel to the beam leads to the formation of a ‘‘shadow cone,’’ thereby reducing the chance of backscattering from atoms deeper into the crystal. This channeling effect provides the surface sensitivity of the method. Ions that are backscattered below the surface cannot penetrate back into the vacuum if they encounter surface atoms. This blocking effect results in pronounced dips in the backscattered angular intensity, and the angular position of these dips is a direct measure of the surface atomic geometry. Monte Carlo ion scattering simulations⁹ of the angular spectra accompanied by an R-factor fitting analysis¹⁰ yield quantitative surface structure information (e.g., layer spacings and vibrational amplitudes). The kinematics of ion scattering provides the mass (and hence chemical) specificity of the technique. Use of Rutherford scattering cross sections, with some screening corrections, leads to quantitative determination of surface coverages to within $\approx 5\%$ (relative error). MEIS has been successfully applied previously to study segregation phenomena.^{11,12}

Figure 1(a) shows a backscattering energy spectrum from the alloy surface after sputtering and annealing to 1000°C for 2 h. This procedure caused the segregation of S and As, both elements being clearly visible. Sn and Nb segregation was barely detected for the annealing conditions used. The S and As signals in the figure correspond to 0.37 ML S and 0.043 ML As [surface concentrations are given in fraction of Fe(100) monolayers]. MEIS is capable of detecting trace amounts of As with a sensitivity at least as low as 0.01 ML. The lack of any substantial W signal is due to a strong surface depletion of this element, and is discussed later. The impurities C, N, and O which are frequently observed on iron based alloy surfaces lie below their detection limits of 0.04, 0.03, and 0.02 ML, respectively.

We have varied annealing temperatures ($800\text{--}1100^\circ\text{C}$) and annealing times (10 min–4 h). Qualitatively our data show the amount of segregated As to increase upon lowering the temperature. However, even at the lowest temperature used here (800°C) desorption of As is very likely (the sublimation temperature of pure As is 603°C), and thus true thermodynamic equilibrium between bulk and surface of the Fe-9%W alloy is almost impossible to establish. Therefore, a plot of As surface coverage versus temperature is meaningless and we present our data in the θ_{As} vs θ_{S} plot of Fig. 1(b). There is a striking linear relationship between these two

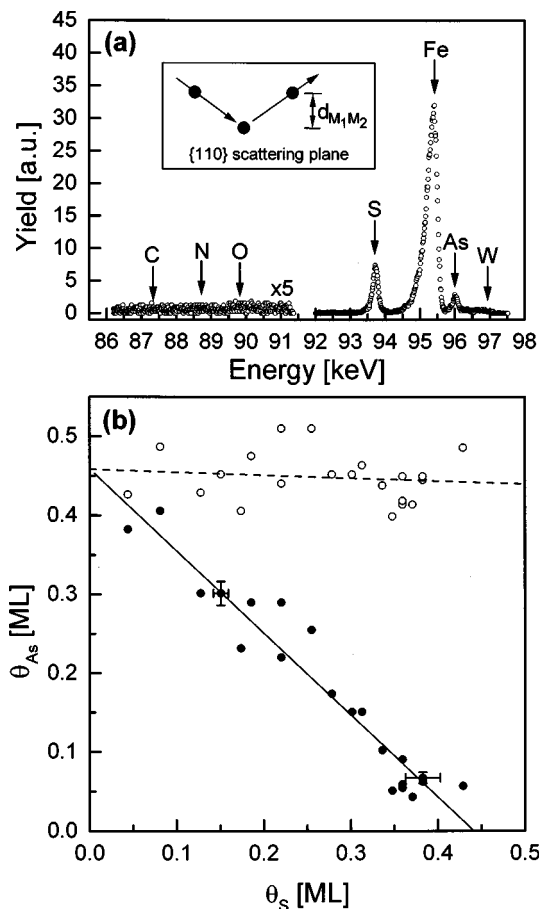


FIG. 1. (a) 98 keV proton backscattering spectrum from the alloy surface in a channeling and blocking configuration in the $\{110\}$ azimuthal plane. The locations of the signal from various surface components are shown. (b) Plot of all the observed As and S coverages after various annealing conditions (solid circles). Site competition of As and S is evidenced by the linear behavior (with slope -1) of the data. The total coverage, $\theta_{\text{As}} + \theta_{\text{S}}$, is also shown (open circles). The lines are least square fits to the data.

quantities, and this clearly indicates that both segregants compete for the available surface sites (site competition). This is consistent with earlier investigations where the site competition of As, S, and P was studied on polycrystalline Fe samples.^{6,7} In all cases the total coverage of both segregants, $\theta_{\text{As}} + \theta_{\text{S}}$, is between 0.40 and 0.51 ML. Low-energy electron diffraction shows $c(2 \times 2)$ patterns with different levels of background intensity for the various surface preparations.

To investigate the possible effects on surface structure due to different relative amounts of S and As, the sample was prepared under two conditions. A sulfur rich surface (0.37 ML S, 0.07 ML As) results from sputtering followed by annealing to 1100°C for 10 min. An arsenic rich surface (0.19 ML S, 0.28 ML As) results from sputtering followed by annealing to 800°C for 20 min, then 980°C for 20 min. Integrating the surface peaks in the energy spectra [Fig. 1(a)] as a function of scattering angle results in angular (blocking) yields. Angular yields from several scattering configurations in the $\{100\}$ and $\{110\}$ azimuthal planes were compared to simulations in order to determine the overlayer-to-metal ($d_{\text{S/As-M}_1}$) and first three metal-to-metal interlayer spacings ($d_{\text{M}_1\text{--M}_2, \dots}$), as well as the W concentration in the first few layers. Overlayer S and As atoms were placed in fourfold-

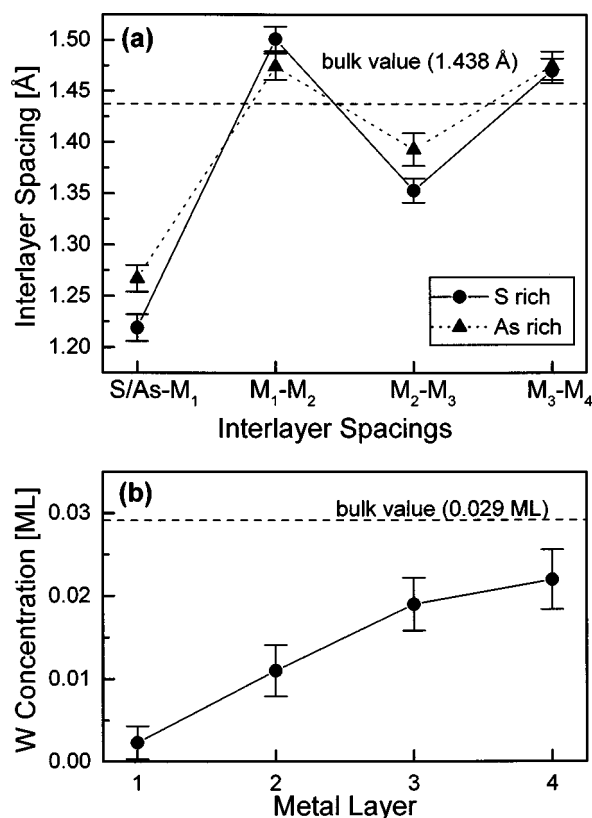


FIG. 2. (a) Interlayer spacings (S/As overlayer to metal distance $d_{S/As-M_1}$, and the first three metal-to-metal layer distances $d_{M_1-M_2}$, $d_{M_2-M_3}$ and $d_{M_3-M_4}$) for S- and As-rich Fe-9%W(100) surfaces. (b) W concentration vs depth for S- and As-rich Fe-9%W(100) surfaces.

hollow $c(2 \times 2)$ sites as has been well established by other methods.^{13,14} No buckling in the S/As overlayer was considered, therefore the results for $d_{S/As-M_1}$ represent an average overlayer-metal distance. Several scattering configurations are used because each is sensitive to various interlayer relaxations.¹⁵

Figure 2(a) shows the interlayer relaxations for the two surface preparations. For the S-rich surface $d_{S/As-M_1}$ is slightly smaller compared to the As-rich surface. This is consistent with the larger atomic radius of As. The metal-to-metal interlayer spacings exhibit oscillatory behavior, with a significant expansion of $d_{M_1-M_2}$, a contraction of $d_{M_2-M_3}$, and again a slight expansion of $d_{M_3-M_4}$ relative to the bulk interlayer spacing of body-centered cubic (bcc) Fe(100). However, these interlayer spacings are not consistent with the angle-resolved photoemission extended fine structure results of Zhang *et al.*,¹⁴ where $d_{M_1-M_2}$ is seen to be contracted and $d_{M_2-M_3}$ expanded for the Fe(100)- $c(2 \times 2)S$ surface. In many earlier studies an adsorbate-induced expansion of $d_{M_1-M_2}$ is seen, for instance for N on Cr(100),¹⁶ for O on Fe(100),^{17,18} for $c(2 \times 2)C/Mo(100)$,¹⁹ and for $c(2 \times 2)N/Fe(100)$.²⁰

Use of several scattering configurations also leads to various numbers of layers being directly visible to the incoming ion beam. Comparing measured angular yields to ion scattering simulations allows the determination of W, As, and S concentrations in these layers. While As and S cannot

be detected except within the uppermost layer, there is a well-pronounced layer dependence of the W concentration. A similar method was applied by Deckers *et al.*¹¹ to study segregation on a PtNi alloy surface. The results for such an analysis on the S-rich surface are shown in Fig. 2(b) (these results are negligibly different for the As-rich surface). S and As segregation clearly leads to a strong depletion of W from the surface region. A possible explanation of this finding are preferential interactions between Fe and S or As.

In summary, the major achievements of this work are the following two points:

- (1) We have given further evidence that MEIS is a powerful technique for studies of surface segregation which combines a high chemical sensitivity with the capability to analyze structural details. MEIS can detect even small amounts of As (≈ 0.01 ML) on metal or alloy surfaces.
- (2) Small amounts of bulk dissolved As (53 wt-ppm) already give rise to a significant As segregation on a (100) oriented Fe-9%W single crystal surface. As segregation has been investigated between 800 and 1100 °C and is accompanied by S segregation. Both elements compete for the available $c(2 \times 2)$ surface sites. With As and S on the surface, there is a strong W depletion of the topmost three metal layers.

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