

CHEMICAL PROFILE ANALYSIS OF TYPE 316 STAINLESS STEEL SHEET BY AUGER SPECTROSCOPY

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Auger electron spectroscopy has been used to determine chemical profiles in type 316 stainless steel. The technique consisted of alternately monitoring Fe, Mo, and Ni Auger peak heights and Ar^+ sputter removal of surface atom layers from stainless steel sheet. The concentration of Mo was found to decrease, whereas the Fe and Ni concentrations increased from the surface into the bulk.

Elemental concentration of solvent or solute atoms do not necessarily remain constant throughout a given sample. Owing to segregation effects the surface concentration of a given component can differ markedly from that of the bulk. Harris (1), Haas (2), and Sickafus (3) have used Auger electron spectroscopy (AES) to show that certain thermal treatments can be used to concentrate bulk impurities at a free surface. Small interstitial impurities, especially those of sulfur and carbon, have been observed to concentrate at the surface after a short time at 300 C (1).

In the present study, AES has been used to determine the concentration profiles of Mo, Ni, and Fe in 316 stainless steel; these were found to vary significantly near the surface.

REVIEW OF AUGER ELECTRON SPECTROSCOPY

The technique of Auger electron spectroscopy (AES) is not new (4), although its application to surface studies is relatively recent (5). The Auger electron emission process is analogous to x-ray emission from an excited atom and, in fact, the processes often occur simultaneously in a given experiment. When an inner core vacancy of an atom is neutralized by absorption of an electron from one of the outer shells either an x-ray or an Auger electron with a precise energy will be emitted from the sample (Fig. 1).

In applying AES to surface studies, the initial inner core vacancy is created by electron bombardment of the surface with 1-3 keV electrons. The secondary Auger electrons coming from within a few monolayers of the surface escape with a well-

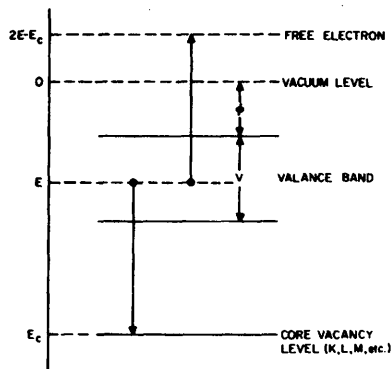


FIGURE 1. Auger electron emission from an excited atom. Φ , work function; V , width of the valence band; E_c , energy of the core electron level; E , original energy of the emitted electron.

defined energy (6). The Auger energy levels of many of the metals and typical surface contaminants are known and the values agree quite well with the x-ray values tabulated by Hill, *et al.* (7)

The interest in Auger spectroscopy as applied to surface studies evolved from the early low energy electron diffraction (LEED) experiments of Lander (8). In analyzing the energy distribution for secondary electrons emitted by a solid surface, he attributed the small peaks to Auger transitions in the solid and suggested that the characteristic energies of these peaks could be used for qualitative surface chemical analysis. The peaks were, however, small and difficult to detect within the broad, rather uniform background distribution. Harris (5) subsequently suggested

that since the background was indeed relatively uniform, detection of Auger peaks could be greatly enhanced by electronically differentiating the energy distribution. This technique brought AES into its current prominence as a valuable tool for surface studies. Subsequent refinements were made by Palmberg (9), who demonstrated that the sensitivity for atoms at the surface could be enhanced by using a grazing incidence primary beam and that the energy resolution could be improved by replacing the old 3-grid LEED optics by a 4-grid system. Palmberg also confirmed experimentally that the low energy (<200 eV) Auger electron escape depth was of the order of 4-8Å. The minimum sensitivity for surface impurities has been estimated to be 0.1 percent of a monolayer (10).

More recently AES experiments are being performed independent of LEED studies. In principle, since the Auger process involves inelastic collisions with the surface, a well-defined crystal geometry, as required by LEED, is not a prerequisite for AES. A new cylindrical mirror analyzer (11) with a coaxial electron gun provides a simple electron optics system with precise energy discrimination. This system can be adapted to most conventional ultrahigh vacuum chambers and AES experiments performed in conjunction with other types of surface studies. An example of the Auger spectra obtained from a stainless steel surface using a Physical Electronics Industries Cylindrical

Analyzer is shown in Figure 2. The various surface components are noted on the trace.

METHODS

Rolled, annealed, and pickled type 316 stainless steel sheet was used in this investigation. Specimens were prepared by washing with detergent, rinsing with distilled water, acetone, trichloroethylene, and acetone, and then drying with a lintfree cloth. Samples were placed in a vacuum chamber, which was evacuated, and then baked 6 hr at 250 C.

Oil-free rough pumping was accomplished by the use of zeolite-filled cryosorption pumps. The pressure was then reduced to the low 10^{-9} torr range with ion and titanium sublimation pumps. Initial Auger spectra were recorded before Ar^+ bombardment as shown in Figure 2. To facilitate sputtering, Ar was admitted to a pressure of 1×10^{-4} torr. Argon purity was maintained by use of titanium sublimation pumps during sputtering. After a predetermined time sputtering was terminated and the system pressure was immediately reduced to the 10^{-9} torr range by activating the ion pumps. The sample was alternately positioned in front of the sputter gun and the cylindrical mirror analyzer by simple rotation.

An Auger spectrum was recorded after each sputter period and then the sample was repositioned for additional sputtering. This procedure was repeated until no change was observed in the recorded spectra. Changes in Auger spectra can be seen readily by comparing a spectrum taken after long-term sputtering to that before sputtering (Fig. 2). The exactness of the repositioning technique is demonstrated by the reproducibility in spectra taken after sufficiently long sputtering time, after having reached the bulk composition (12).

RESULTS

The Auger spectra for pure samples of the elements of interest were used to determine the locations of the peaks monitored for this study. As an example, the spectrum for pure Mo is shown in Figure 3. It was assumed that the Auger spectra obtained after long sputtering times were representative of the bulk concentration.

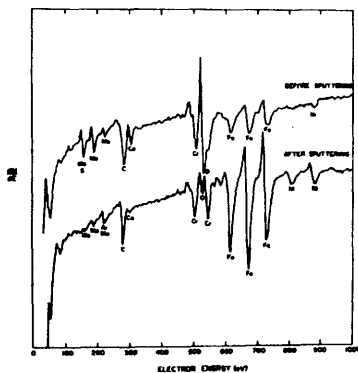


FIGURE 2. a) Auger electron spectrum of type 316 stainless steel before sputtering; $V_B = 2000$ eV, b) Auger electron spectrum of 316 stainless steel after sputtering; $V_B = 2000$ eV.

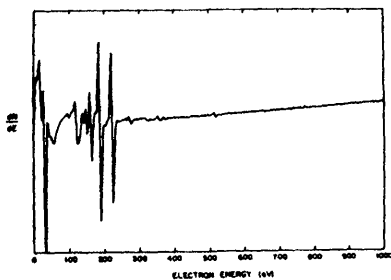


FIGURE 3. Auger electron spectrum of pure molybdenum; $V_B = 2000$ eV.

A removal coefficient of unity (one atom removed for each incident argon ion) was assumed and, by taking the Auger peak height to be directly proportional to the atomic density present (13), the surface concentration could be estimated. A composite of the chemical profiles obtained for Mo, Fe, and Ni is shown in Figure 4. These

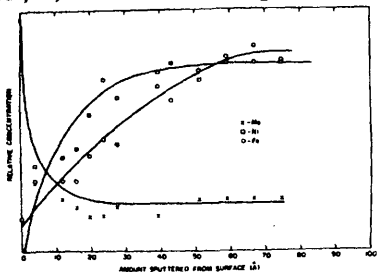


FIGURE 4. Relative molybdenum, nickel, and iron concentrations vs amount of material removed in type 316 stainless steel.

assumptions resulted in an estimated surface concentration of 14%, 15%, and 0% for Mo, Fe, and Ni, respectively. The pretreatment and cleaning steps left a carbonaceous over-layer on the surface (14) which may have somewhat reduced the true concentration of metallic surface species.

Significant variation in the chemical profiles of Mo, Fe, and Ni near the surface

of mill-processed type 316 stainless steel sheet was observed. The Mo concentration was found to decrease as surface layers were removed by Ar^+ bombardment, while the Fe and Ni concentrations increased until the bulk concentrations were reached.

CONCLUSIONS

It was found that mill-processing tends to produce a variation in chemical profiles of Mo, Fe, and Ni at the surface of type 316 stainless steel. Since the segregation or depletion is apparently brought about by the mill-processing, subsequent thermal or mechanical processing probably results in a change in the chemical profiles. Thus, any property, such as corrosion resistance, that is dependent on surface composition could be significantly altered. Chemical profiles obtained by AES should be of great assistance in interpreting experimental results of investigations involving surface-sensitive properties.

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