

XPS INVESTIGATIONS OF Fe-Ni ALLOYS*

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The electronic structure of Fe-Ni alloys was investigated by X-ray photoelectron method. The notable shifts of Ni $2p_{3/2}$ and Fe $2p_{3/2}$ core levels are described. It was found that the FWHM's of the XPS valence band spectra in Fe-Ni alloys decrease with an increase in the Ni concentration.

1. Introduction

In several recent publications of Fe-Ni alloys some aspects of their electronic structure as the valence band structure, the density of electron states at the Fermi level and the core electron binding energies have been investigated. The strong dependence of the magnetic behaviour and electronic specific heat of Fe-Ni alloys on the concentration stimulates such works. The theoretical calculations of the electron band structure of Fe-Ni alloys in both the bcc and fcc phases were done by Hasegawa and Kanamori [1, 2]. They found nonlinear changes in the density of electron states at the Fermi level for the fcc range of concentrations and only slight changes of the valence band width in the entire concentration range.

The lattice constant in alloys is larger than the lattice constant of pure Ni. For example, $a = 3.5522 \text{ \AA}$ for Ni_3Fe and $a = 3.5238 \text{ \AA}$ for Ni. The results of Heine's [3] theoretical investigations showed that if the lattice spacing increases then band narrowing can occur. Wandelt and Ertl [4] using the appearance potential method did not find any nonlinear detectable change in the density of electron states at the Fermi level for the entire concentration range. They reported only the $2p$ electron binding energy shifts which occurred for Ni $2p$ levels in Fe-Ni alloys. Hague et al. [5] investigated the electron valence bands and the core electron levels of pure Ni and Fe as well as ordered and disordered Ni_3Fe alloys

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using X-ray photoelectron spectroscopy and soft X-ray spectroscopy. They found that the Fe $2p_{3/2}$ photoelectron line and the Fe L_3 X-ray emission spectrum for the alloys were broadened compared to that of pure Fe. Also the Ni L_3 spectrum for the alloys was broader than in pure Ni. The Ni $2p_{3/2}$ photoelectron line was unchanged. The XPS valence band spectra of the alloys were broader than for pure Ni, but narrower than for pure Fe. The XPS measurements of the Fe $2p$ levels for Fe₈₀Ni₂₀ and Fe₇₀Ni₃₀ alloys were performed by Berndt et al. [6]. They also found these photoelectron lines to be broader than in pure Fe. In other words, these experimental investigations have revealed that the broadening of the valence band occurs instead of the narrowing predicted by theory.

The purpose of this paper is to investigate the changes in the electronic structure of Fe-Ni alloys in the entire concentration range using the X-ray photoelectron method.

2. Results and discussion

The spectrometer used (GCA McPherson ESCA 36) is an instrument with the spherical analyser without a retarding field. For this type of spectrometer the resolution is given by $\Delta E/E = \text{constant}$ and the experimentally determined photoelectron energies require a relativistic correction (Ebel [7]). The calibration of the energy scale was defined by the binding energy of Au $4f_{7/2}$ electrons as 84.00 eV. The Mg K_α radiation ($h\nu = 1253.6$ eV) from an X-ray tube operated at 7 kV, 40 mA was used for excitation. A combination of rotary pump, turbomolecular pump and cryopump kept the vacuum in the sample chamber well below 10^{-6} Pa.

The Fe-Ni alloys have been prepared by melting pure Ni (99.99%) and pure Fe (99.99%) under an argon atmosphere in an induction furnace. From the bulk material the 0.1 mm foils were obtained by cold rolling. The homogeneity was controlled by electron microbeam analysis. The structural phases were examined by the X-ray diffraction method. The surface was polished with 0.3 μm $\alpha\text{-Al}_2\text{O}_3$ powder. Oxide layers on the surface were removed by argon ion sputtering inside the sample chamber. From a comparison of the intensity of Fe $2p_{3/2}$ and Ni $2p_{3/2}$ photoelectron lines before and after sputtering, the effect of selective sputtering can be neglected. The $2p_{3/2}$ lines were chosen because of their low FWHM's (full widths in half maximum) and high intensities. The valence band photoelectron spectra also were measured.

The results are summarized in Fig. 1. The values of the measured binding energies of electrons in the alloys investigated are listed in Table I. The error in binding energy can be estimated as less than ± 0.2 eV. These findings compared with those of Hague et al. [5] and Berndt et al. [6] are in good agreement. The systematically higher values for the Fe $2p_{3/2}$ binding energies compared to the results of Hague et al. can be explained by the different evaluation procedures. The systematic increasing in the FWHM of the Fe $2p_{3/2}$ photoelectron line with increasing Ni concentration observed in the alloys also agrees with the results of Hague et al. [5] and Berndt et al. [6]. The results show that the core level binding energies of both components in the Fe-Ni system shift to higher binding energies upon alloying. Usually such a shift indicates a decrease in electron density at an atomic site. This is not possible for both components in terms of a charge transfer since both sites

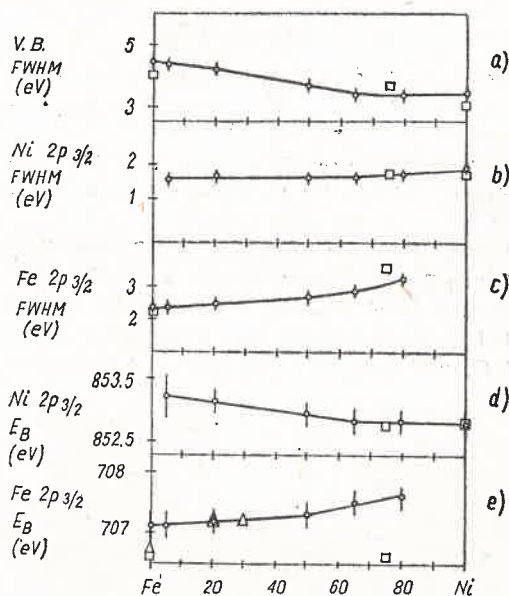


Fig. 1. XPS measurements as a function of Fe-Ni concentration. (a) FWHM of the valence band spectrum; (b), (c) FWHM's of $2p_{3/2}$ photoelectron lines; (d), (e) binding energies of $2p_{3/2}$ electrons. Results of Hague et al. [5] are indicated by squares and the results of Berndt et al. [6] by triangles

TABLE I

Binding energies of Fe $2p_{3/2}$ and Ni $2p_{3/2}$ electrons in Fe-Ni alloys (in eV)

Alloy	Fe $2p_{3/2}$	Ni $2p_{3/2}$	Phase
Fe	707.1	—	bcc
Fe ₉₅ Ni ₅	707.1	853.2	bcc
Fe ₈₀ Ni ₂₀	707.2	853.1	bcc
Fe ₅₀ Ni ₅₀	707.3	852.9	fcc
Fe ₃₅ Ni ₆₅	707.5	852.8	fcc
Fe ₂₀ Ni ₈₀	707.6	852.8	fcc
Ni	—	852.7	fcc

must become positively charged. A similar effect was observed by Fuggle et al. [8] in aluminium-noble metal alloys. They suggested following Watson and Perlman [9], in that there was no unique way to draw atom boundaries, and that if an atom's valence shell was to expand in some way, the observed core-level shift would be the same as if charge was transferred from the atom.

Our results show that the FWHM of XPS valence band spectra in Fe-Ni alloys increases with increasing Fe concentration in the Fe concentration range from 35 to 80 percent which is in contradiction to theoretical concepts [1, 3]. This can be explained by the overlapping of valence bands of Fe and Ni in this concentration range. However, this effect also can be due to the large difference in photoionization cross-sections of d -electrons which is about two times greater for Ni than for Fe in both components [10].

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