

Fe-Ni Alloys studied by XPS

Nobuya Okude, Mikio Furuya*, and Metal Materials Group of SASJ**

Applied Technology Research Center, NKK Corporation, 1-1 Minamiwatarida-cho, Kawasaki-ku, Kawasaki 210-0855, Japan

**Kanagawa Industrial Technology Research Institute, 705-1 Shimoimaizumi, Ebina 243-0435, Japan*

***The Surface Analysis Society of Japan, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*

(Received September 30 1998; accepted January 13 1999)

The XPS spectra for Fe-Ni alloys by two organizations have been investigated. The change of the O 1s spectrum for the as-received surface with the changes of the concentration and the crystal structure and the shift of the Ni 2p_{3/2} satellite peak for the ion-sputter-cleaned surface with the change of the concentration are observed. The surface concentrations estimated for as-received and ion-sputter-cleaned surfaces coincide with the bulk values in a few percent deviation if proper pairs of peaks are used.

1. Introduction

In order to clarify the problem on studying alloy surfaces using Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS), round robin tests using Fe-Ni alloys have been carried out by Metal Materials Group of the Surface Analysis Society of Japan. In the case of these alloys, compared with Au-Cu and Co-Ni alloys used in the previous round robin tests [1], [2], [3], the difference in the character of between each atom, for example the electrochemistic character, is bigger, and the crystal structure changes with the variety of the atomic concentrations, which is the main reason for choosing Fe-Ni alloys for our collaborations. In this tests, as-received surfaces as well as clean surfaces have been paid attention, because the quantitative analysis of substrate atoms for contaminated and oxidized surfaces are also requested in surface analysis of practical materials. In the present paper, the XPS spectra for as-received and ion-sputter-cleaned surfaces of Fe-Ni alloys measured by two organizations and the accuracy of quantitative analysis using XPS will be discussed.

2. Experimental

Fe-Ni alloys, which were prepared by the following process: (1) arc melt, (2) anneal at 1050°C for 1 hour, (3) hot roll above 950°C, (4) cut into pieces (10mm x 10mm), (5) mirror polish, were presented by SUMITOMO METAL INDUSTRIES. LTD. The specimens were degreased with acetone before XPS measurements. Table 1 shows the chemical compositions of Ni and the crystal structures of

the alloys which were confirmed using x-ray diffraction technique at KOBELCO RES. INST.

Table 1 Chemical compositions and crystal Structures of Fe-Ni alloys.

Sample No.	Ni (mass%)	crystal structure
101	<0.01	bcc
105	19.7	bcc
107	49.3	fcc
108	69.4	fcc
100	99.2	fcc

The XPS measurements were carried out using SSX-100 (SSI) with monochromatized Al K α radiation at NKK Corporation and ESCA-5500 (PHI) spectrometer with non-monochromatized Al K α radiation at Kanagawa Industrial Technology Research Institute. The binding-energy scales were calibrated so that the binding energies of Au 4f_{7/2} correspond to 84.0 eV. The detection angles of the photoelectrons were 50 and 45 degrees from the surface normal, respectively.

The calculations of surface concentrations of Fe and Ni were carried out using (i) Fe 3p and Ni 3p and (ii) Fe 3p and Ni 2p_{3/2} peaks in two ways : (i) using relative sensitive factors for each instruments ("Relative sensitive factor" method [3]), (ii) using the intensities of the peaks for ion sputter-cleaned surfaces of the Fe-Ni alloys of 0 and 99.2 mass% of Ni as standards without the correction using matrix factors ("Pure metal standard" method [3]). In the case of as-received surfaces, total

intensities, the sum of the intensities of the peaks originated from metallic and oxide states, were used. The reason why Fe 2p_{3/2} peaks were not used was that the intensities were not able to be estimated due to the overlaps of Ni LMM Auger lines.

3. Results and discussion

3.1 XPS spectra for as-received surfaces

Oxide layers and contaminated layers on as-received surfaces of Fe-Ni alloys thinner than escape depths of Fe 2p and Ni 2p photoelectrons were confirmed by Fe 2p and Ni 2p spectra. In O 1s spectra for the layers measured using SSX-100 spectrometer (Fig. 1), two peaks are observed for every samples. The lower-binding-energy peak (~530eV) and the higher-binding-energy peak (~532eV) are originated from -O and -OH, respectively [4]. The ratio of the intensity of each peak to the total intensity as a function of bulk Ni content is shown in Fig. 2. The ratio of the lower(higher)-binding-energy peak decreases (increases) with the increase of Ni content in spite of the almost constant surface concentration of O calculated, which means that the hydroxide can be formed easier than the oxide on Fe-Ni alloys of higher Ni content. That would be because the Gibbs free energy (-477.3 kJ mol⁻¹) of Ni(OH)₂ is smaller than that (-211.7 kJ mol⁻¹) of NiO [5]. It is, therefore, concluded that Ni forms mainly Ni-OH and Fe forms Fe-O and Fe-OH. On the other hand, it

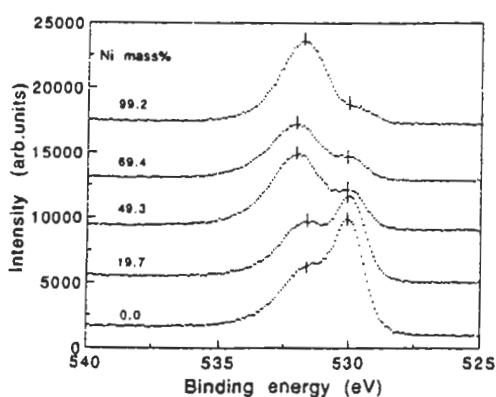


Fig.1 O 1s spectra for as-received Fe-Ni alloys. (Ni : 0, 19.7, 49.3, 69.4, 99.2 mass%)

is interesting to notice that the ratio changes with a discontinuity between 19.7 and 49.3 mass% of Ni. The discontinuous change means that the surface oxide state depends on not only the concentration but also the crystal structure which would affect the surface free energy.

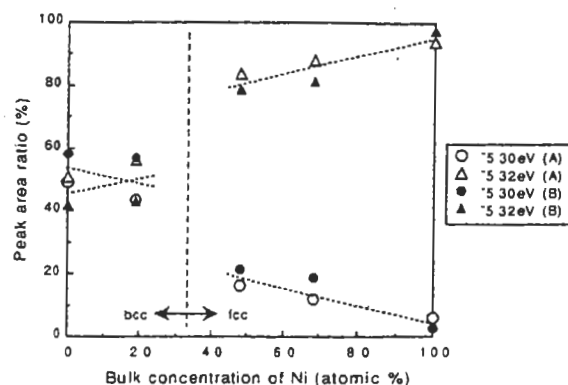


Fig.2 Peak area ratios of O 1s peaks (at ~530eV and ~532eV) for as-received Fe-Ni alloys as a function of the bulk concentration of Ni. (A : SSX-100, B : ESCA-5500)

3.2 XPS spectra for ion-sputter-cleaned surfaces

In Ni 2p spectra for ion-sputter-cleaned surfaces of Fe-Ni alloys measured using SSX-100 spectrometer (Fig.3), the Ni 2p_{3/2} main peak (~852eV) does not move, whereas the Ni 2p_{3/2} two-hole satellite peak (~858eV) shifts to the higher-binding-energy side with the decrease of bulk Ni content. The difference of the binding energies of between Ni 2p_{3/2} main and satellite peak as a function of Ni content is shown in Fig.4. It is noticed in the figure that the difference grows with the decrease of Ni content and seems to saturate at about 50 atomic% of Ni. The behavior of the satellite peak is similar to that for some other alloys such as Ce-Ni [6] and Zn-Ni [7]. Such behavior had been attributed to the charge transfer from partner elements to Ni 3d [6], [7], therefore, in this system, the charge transfer from Fe to Ni 3d would also affect the position of the satellite peak. The similar continuous shifts were also observed in Fe 2p and valence-band spectra, which can be related to the charge transfer.

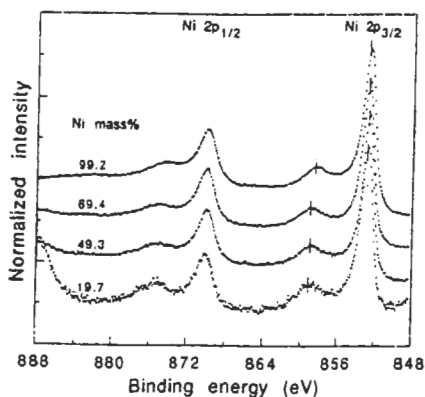


Fig.3 Ni 2p spectra for ion-sputter-cleaned Fe-Ni alloys. (Ni : 0, 19.7, 49.3, 69.4, 99.2 mass%)

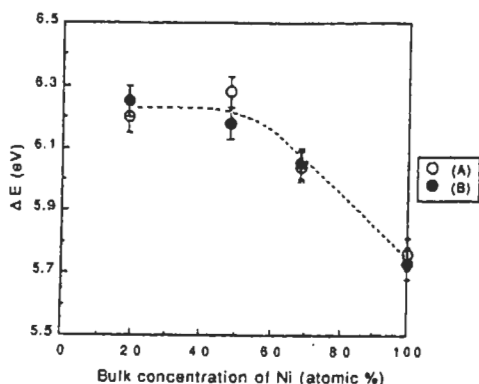


Fig.4 Binding-energy difference between Ni 2p_{1/2} main and satellite peak for ion-sputter-cleaned Fe-Ni alloys as a function of the bulk concentration of Ni. (A : SSX-100, B : ESCA-5500)

3.3 Quantitative analysis of surfaces

The surface concentrations of Ni for as-received and ion-sputter-cleaned surfaces of Fe-Ni alloys as a function of the bulk concentration of Ni are shown in Fig.5. Open and solid plots represent the results of the calculations carried out using (i) Fe 3p and Ni 3p and (ii) Fe 3p and Ni 2p_{3/2} peaks, respectively. In Fig.5 (a) for as-received surfaces, it is noticed that, in spite of the above mentioned change of the surface oxide state, the surface concentrations estimated using Fe 3p and Ni 3p peak intensities are in good agreement with the bulk values. On the other hand, those estimated using Fe 3p and Ni 2p_{3/2} peak intensities are remarkably lower than the bulk values. The deviation can be attributed to the difference in the sampling depths between the two peaks used because those photoelectrons have different kinetic energies. The Ni concentration in the sampling depth would be reduced due to the surface contamination layer and/or an enrichment of Fe in the surface oxide

layer which was confirmed by Fe 2p and Ni 2p spectra. For ion-sputter-cleaned surfaces (Fig.5 (b)), in every type of estimations, the surface concentrations coincide with the bulk values in a few percent deviation. This indicates that the depth distribution of the concentrations are uniform in the sampling depths and the preferential sputtering, which is a serious problem in the surface analysis of any other alloy systems, is very small in this system. The deviation is smaller than in the case of Au-Cu alloys [3], which shows that matrix effects are almost negligible in this system because of close atomic number of Fe and Ni.

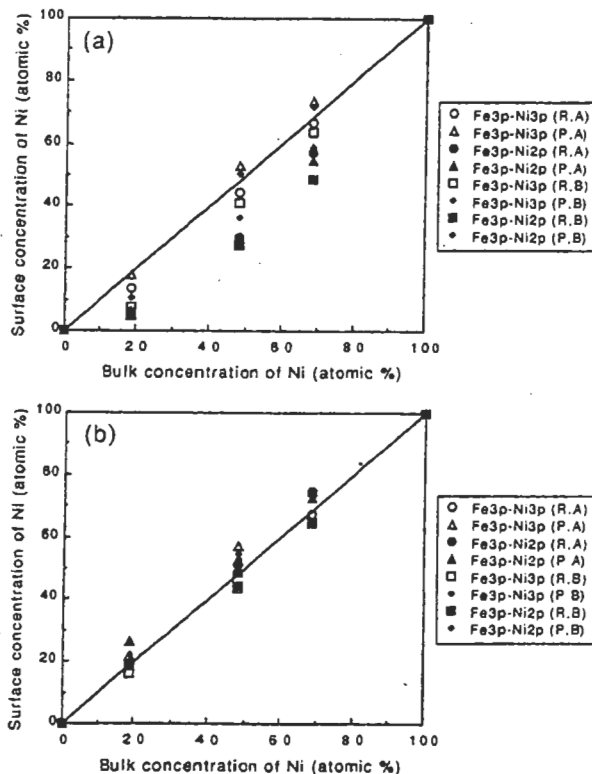


Fig.5 Surface concentration of Ni (Fe+Ni=100%) for (a) as-received and (b) ion-sputter-cleaned Fe-Ni alloy as a function of bulk concentration of Ni. (R : "Relative sensitive factor" method, I : "Intensity of standard" method, A : SSX-100, B : ESCA-5500)

4. Conclusion

The characteristics of XPS spectra and the estimated surface concentrations for Fe-Ni alloys were in good agreement between two organizations. The O 1s spectrum for as-received surface changes with the change of not only the concentration but also the crystal structure. The Ni 2p_{3/2} satellite peak for ion-sputter-cleaned surface shifts with the change of the concentration. The surface concentrations can be estimated by XPS for ion-sputter-cleaned surfaces in a few percent deviation, which indicates that the preferential sputtering is negligible in this system. For as-received surfaces, the concentrations can be estimated if Fe 3p and Ni 3p peaks are used.

Acknowledgment

The authors would like to thank Dr. Usuki and Dr. Arai at SUMITOMO METAL INDUSTRIES. LTD. for providing Fe-Ni alloys and useful information about them.

References

- [1]K. Yoshihara et al., Surf. Interf. Anal. **12**, 125(1988).
- [2]K. Yoshihara et al., Mater. Japan **30**, 595(1991). [in Japanese.]
- [3]M. Yoshitake, K. Yoshihara, and other member of the VAMAS-SCA working group in Japan, Surf. Interf. Anal. **17**, 711(1988).
- [4]C.D.Wagner et al. Ed., Handbook of X-ray photoelectron spectroscopy, (Perkin-Elmer Corporation).
- [5]S.Iizumi Ed., *Kagakubinran* 2nd. Ed. (Maruzen Corporation), p.962. [in Japanese.]
- [6]F. Ulrich Hillebrecht et al., Phys. Rev. B **27**, 2179(1983).
- [7]M. Nagoshi and A. Miyamoto, J. Surf. Sci. Soc. Jpn. **17**, no. 5, 282(1996).