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The Surface Tension of Undercooled Binary Iron and Nickel Alloys and the Effect of Oxygen on the Surface Tension of Fe and Ni[1]

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The surface tension of the undercooled binary alloys, iron–nickel and nickel–cobalt, was measured as a function of composition and temperature using the oscillating droplet method combined with electromagnetic levitation. The measurements cover a wide temperature range, including the overheated as well as the undercooled regime. In addition, the effect of oxygen on the surface tension of the elements, iron and nickel, has been determined. When exposed to an oxygen/helium gas flow of constant composition and flux, the surface tension decreases exponentially with increasing exposure time. The oxygen content in the gas mixture was monitored by a gas analyzer using a zirconia transducer. In addition, the amount of oxygen in the sample was determined by X-ray photo-electron-spectroscopy (XPS) before the experiment as well as for processed samples.

KEY WORDS: electromagnetic levitation; effect of oxygen; iron–nickel alloy; nickel–cobalt alloy; surface tension.

1. INTRODUCTION

The primary aim of this study is to measure the surface tension, as an important physical property, of undercooled binary alloys over a wide temperature range and as a function of composition. Fe, Ni, Co, and their alloys form the basis of steel-making. While alloys of industrial relevance are usually multicomponent systems, we have chosen to study the binary alloys, Fe–Ni and Ni–Co, for the sake of clarity. Since surface phenomena involving surface-active elements play an important role in metallurgical

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and technical processes, we also try to determine the influence of oxygen, as a highly surface active element, on the surface tension. For example, Keene [1] has reported that during TIG (tungsten inert gas) welding of steels, certain alloys occasionally exhibit irregular welding characteristics. The reason for the unpredictible welding behavior arises from differences in surface properties of the melts resulting from variations in surface-activity impurity levels. Just small traces of oxygen can exert a dramatic effect on the value of the surface tension [2].

We used the electromagnetic levitation technique combined with the oscillating droplet method to measure the surface tension of the binary alloys, Fe–Ni and Ni–Co, and to study the effect of oxygen on the surface tension of iron and nickel. This technique avoids any contact with substrate material and overcomes the contamination problem of specimens. Therefore, large undercooling levels become possible.

2. MEASUREMENT TECHNIQUE

The principal idea of the so-called oscillating droplet method is the relationship between the oscillation frequency and the surface tension of a levitated liquid and spherical droplet derived by Lord Rayleigh [3]:

$$\gamma = \tfrac{3}{8}\pi M\omega_{l=2}^2 \qquad (1)$$

where γ is the surface tension of the liquid, M is the mass of a droplet, and $\omega_{l=2}$ is the oscillation frequency of the fundamental mode $l=2$. Under real experimental conditions on earth, the Rayleigh frequency splits into five unequally spaced peaks caused by an aspherical equilibrium shape and rotation of the oscillating droplet. This problem has been solved by Cummings and Blackburn [4]. They have derived the following frequency sum rule to calculate the surface tension:

$$\gamma = M\frac{3}{32\pi}\left[\sum_{m=-2}^{2}\omega_{2,\mathrm{m}}^2 - \omega_\tau\left(1.9 + 1.2\frac{z_0^2}{R^2}\right)\right] \qquad (2)$$

with

$$z_0 = \frac{g}{2\omega_\tau^2} \qquad (3)$$

where ω_τ is the translation frequency, R is the radius, and g is the gravitional acceleration. The reliability of the correction formula was confirmed by measurements on ground and in space [5]. The surface tension values obtained under microgravity, where the Rayleigh formula is applicable, are in good agreement with ground-based data calculated according to Eq. (2).

For binary alloys, the surface tension can be expressed by Butler's formula [6].

$$\gamma = \gamma_1 + \frac{\mu^i_{1,\,\text{mix}} - \mu^B_{1,\,\text{mix}}}{A_1} = \gamma_2 + \frac{\mu^i_{2,\,\text{mix}} - \mu^B_{2,\,\text{mix}}}{A_2} \tag{4}$$

where $\mu^i_{1,\,\text{mix}}$, $\mu^B_{1,\,\text{mix}}$, $\mu^i_{2,\,\text{mix}}$, and $\mu^B_{2,\,\text{mix}}$ represent the mixing contributions to the chemical potentials of species 1 or 2 at the interface i or bulk B. A_1 and A_2 represent the molar surface areas of species 1 and 2.

The effect of mixing on the chemical potentials can be divided into two parts: the ideal mixing behavior of purely entropic origin and the nonideal behavior $\delta\mu$ due to interaction:

$$\mu_{\text{mix}} = kT \log c + \delta\mu \tag{5}$$

A number of models have been developed for $\delta\mu$, e.g., the regular and subregular solution models [7].

The effects of surface-active species on the surface tension of liquid metals and alloys are important in numerous industrial applications [2, 8–12]. Belton [13] used a combination of Gibbs and Langmuir adsorption isotherms to derive a formalism which describes the surface tension of a liquid metal in presence of a surface active element:

$$\gamma^o - \gamma = RT\Gamma_S \ln[1 + Ka_i] \tag{6}$$

where γ^o is the surface tension of the pure metal, R is the gas constant, Γ_S is the surface excess concentration at saturation, K is the adsorption coefficient, and a_i is the activity of species i in solution. The equilibrium constant K can be expressed in two components and is given by:

$$K = e^{-(\Delta S^o/R)} e^{-(\Delta H^o/RT)} = k_1 e^{-(\Delta H^o/RT)} \tag{7}$$

where k_1 is a constant which is related to the entropy of segregation, and ΔH^o is the standard heat of adsorption.

Combining this with the temperature dependence of the surface tension of the pure metal, we get a relation for the surface tension as a function of temperature and solute activity:

$$\gamma = \gamma^o_{\text{m}} + \frac{\partial \gamma}{\partial T}(T - T_{\text{m}}) - RT\Gamma_S \ln[1 + k_1 a_i e^{-(\Delta H^o/RT)}] \tag{8}$$

In this equation γ_{m}^{o} is the surface tension of the pure metal at the melting temperature. With this formula (6) we can estimate the surface tension of liquid metals containing oxygen.

Furthermore, the amount of oxygen on the solid sample surface can be determined by XPS as well as by Auger analysis. By using the argon ion sputtering technique, we can also obtain a depth profile of the sample surface.

3. EXPERIMENTS AND RESULTS

The apparatus for surface tension measurements including the effect of oxygen on the surface tension consists of a small ultrahigh vacuum levitation chamber and an optical system as shown in Fig. 1. The levitation coil, in which the pure elements were levitated and alloyed, was powered by a 25 kW high-frequency generator operating at 490 kHz. For the contactless temperature measurement, a single-color pyrometer was used, calibrated at the melting temperature. The pyrometer covers a temperature range from 550 to 2000°C at one wavelength and looks at the sample from the top over a mirror system. During the experiments the sample temperature was

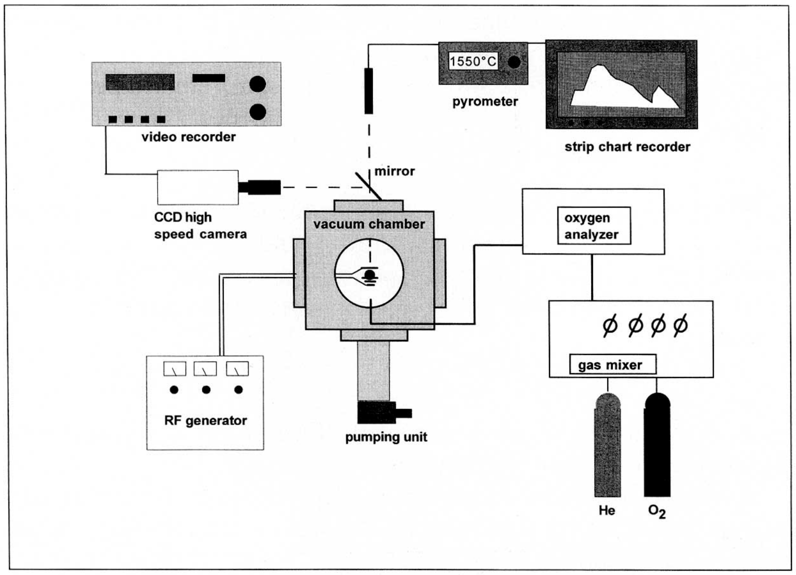

Fig. 1. Schematic diagram of the experimental arrangement to determine the surface tension of molten alloys by the electromagnetic oscillating drop technique and to measure the effect of oxygen on the surface tension.

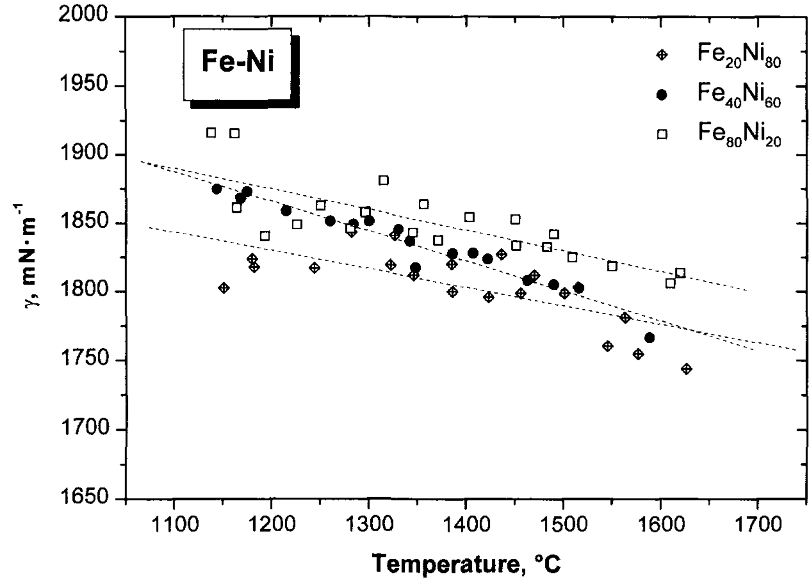

Fig. 2. Surface tension of Fe–Ni alloys as a function of temperature.

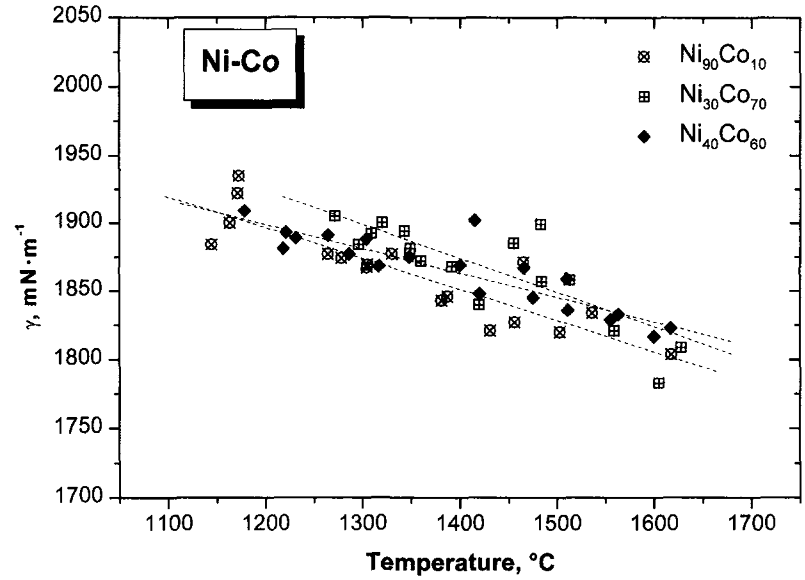

Fig. 3. Surface tension of Ni–Co alloys as a function of temperature.

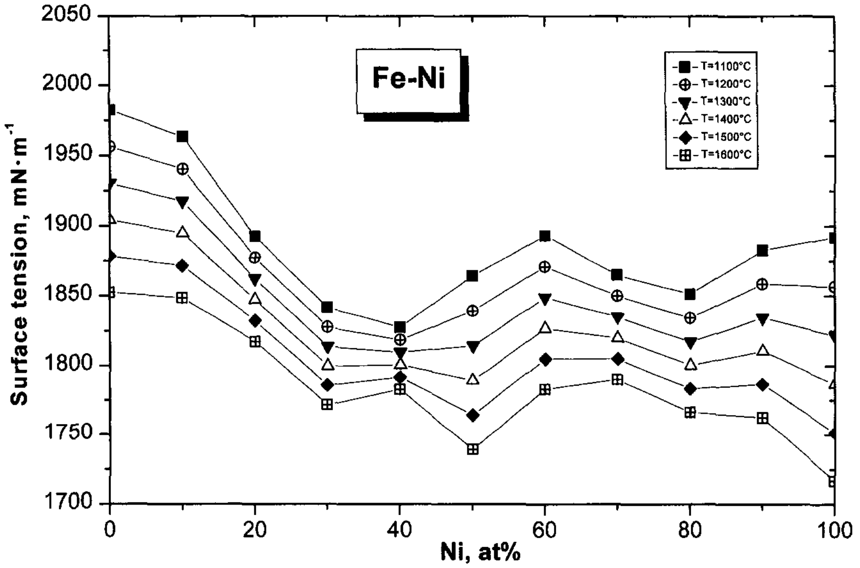

Fig. 4. Surface tension of Fe–Ni alloys as a function of concentration.

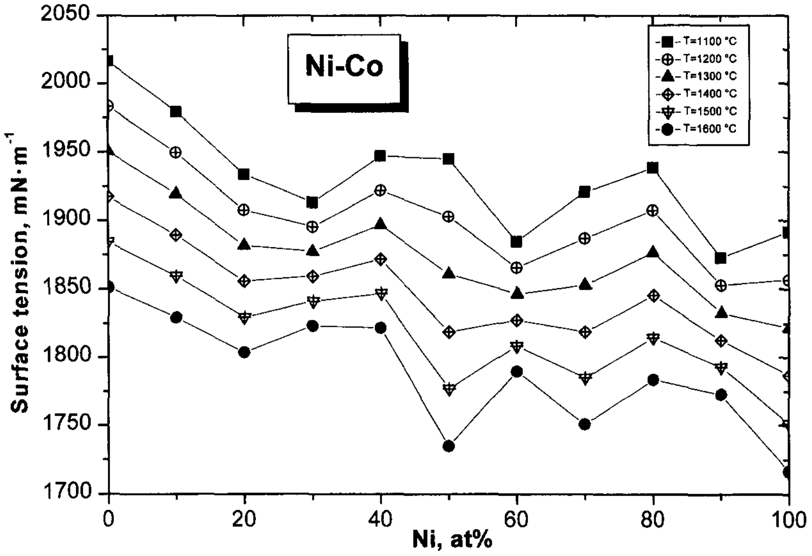

Fig. 5. Surface tension of Ni–Co alloys as a function of concentration.

controlled and maintained by varying the gas flow through the sample holder. The gases used were highly pure He/H_2 (99.9999%) for the surface tension measurement and a mixture of He (99.999%) and O_2 (99.999%) for the oxygen measurements. For the recording of the surface oscillation of the liquid specimen (≈ 50 Hz), a high-speed CCD video camera was used at 100 Hz. It takes images of the sample from the top. The acquired images were recorded on videotapes.

For the oxygen measurements the levitation facility was combined with a Xentra 4100 gas purity analyzer. By using a zirconia oxygen sensor it makes accurate oxygen measurements from trace level (1 vpm) to 100%.

An image processing system [14] evaluates the time dependence of the cross section a, the horizontal radius $R(0°)$, and the perpendicular radius $R(90°)$ of the sample. In addition, the translation of the center of the mass in two directions is also analyzed. A Fourier transformation supplies the frequency spectrum up to 50 Hz. By using the sum rule [Eq. (2)], we obtained the surface tension at the selected temperature. In this way, we got values for the variation of the surface tension of iron–nickel and nickel–cobalt alloys as a function of temperature (Figs. 2 and 3) and concentration (Figs. 4 and 5). The temperature dependence of the surface tension of the alloys Fe–Ni and Ni–Co can be fitted by a linear relation:

$$\gamma(T) = \gamma_m^o + \frac{\partial \gamma}{\partial T}(T - T_m) \qquad (9)$$

with negative temperature coefficients $\partial\gamma/\partial T \leqslant 0$, as expected. The parameters for the respective fits are shown in Tables I and II.

The concentration dependence of the surface tension shows nonlinear behavior for both alloys. This has been observed in other binary alloys as well, e.g., in Cu–Ni by Gorges [13]. Such a behavior can be explained by a subregular solution model.

Table I. Experimental Parameters for the Linear Surface Tension Relation [Eq. (9)] of Fe–Ni

Composition	γ_m^o (mN · m^{-1})	$d\gamma/dT$ (10^{-4} N · mK^{-1})	T_m (°C)
Fe	1869	−0.26	1536
Fe_{20}–Ni_{80}	1991	−0.13	1443
Fe_{40}–Ni_{60}	2127	−0.22	1440
Fe_{80}–Ni_{20}	2056	−0.15	1475
Ni	1768	−0.35	1453

Table II. Experimental Parameters for the Linear Surface Tension Relation [Eq. (9)] of Co–Ni

Composition	γ''_{m} (mN · m^{-1})	$d\gamma/dT$ (10^{-4} N · mK^{-1})	T_{m} (°C)
Ni	1768	−0.35	1453
$\mathrm{Ni_{90}}$–$\mathrm{Co_{10}}$	1801	−0.20	1459
$\mathrm{Ni_{30}}$–$\mathrm{Co_{70}}$	1845	−0.18	1479
$\mathrm{Ni_{40}}$–$\mathrm{Co_{60}}$	1853	−0.25	1475
Co	1886	−0.33	1495

We have also determined the effect of oxygen on the surface tension of the pure elements, iron and nickel. The specimens were levitated and overheated up to 300°C above the melting temperature in a He/H_2 environment. The initial oxygen content on the sample surface was reduced according to the reaction

$$\mathrm{MeO} + \mathrm{H_2} \leftrightarrow \mathrm{Me} + \mathrm{H_2O} \qquad (10)$$

The specimen was immediately solidified by increasing the flow rate of the gas and kept for XPS analysis. Figures 8a and 9a show the results of this

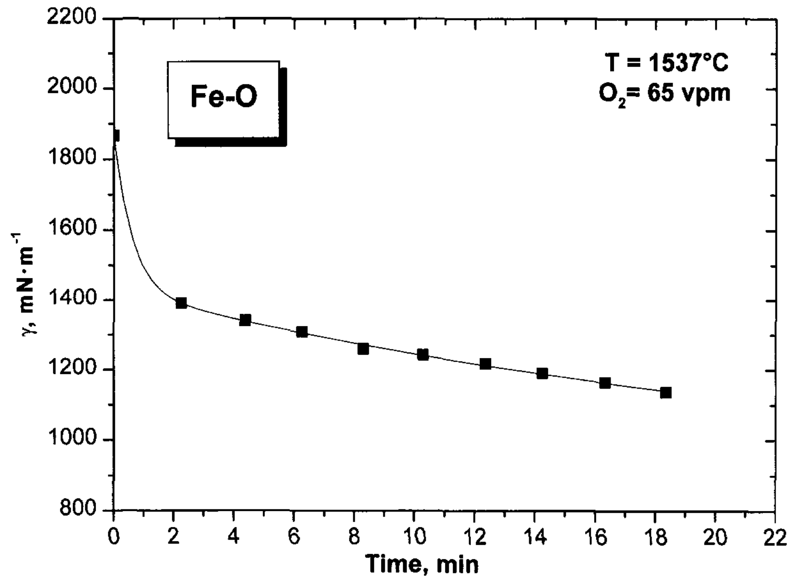

Fig. 6. The effect of oxygen on the surface tension of iron.

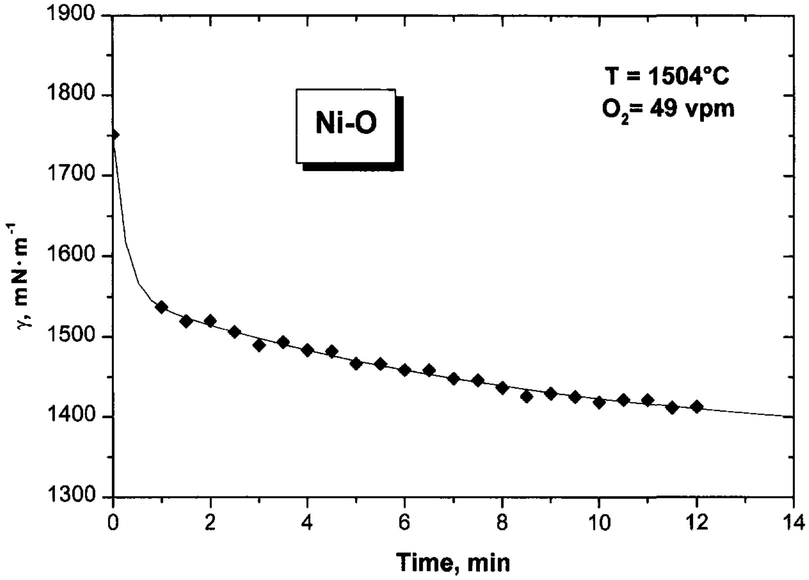

Fig. 7. The effect of oxygen on the surface tension of nickel.

analysis. Oxygen peaks are barely visible, while the metal peaks from either iron or nickel (Auger peaks and 2*p* absorption peaks) are pronounced. After analysis the sample was levitated in an adjusted He/O_2 gas flow at a constant temperature. The surface oscillations were recorded as a function of time. Figures 6 and 7 show that the surface tension values decrease with increasing time. The results were fitted by an exponential curve:

$$\gamma(\text{Fe–O}, t) = 852 + 443e^{-1.61t} + 571e^{-0.04t} \quad (11)$$

$$\gamma(\text{Ni–O}, t) = 1361 + 197e^{-4t} + 193e^{-0.14t} \quad (12)$$

After measuring the surface tension, we kept the samples for a second XPS measurement. The results of these XPS measurements are shown in Figs. 8b and 9b.

4. CONCLUSION AND FUTURE PLANS

This work presents measurements of the surface tension of undercooled binary iron–nickel and nickel–cobalt alloys over a wide temperature range as a function of the concentration. Furthermore, it presents a study of the influence of oxygen on the surface tension of iron and nickel. The results for the pure elements, Fe, Ni, and Co, are in good agreement with

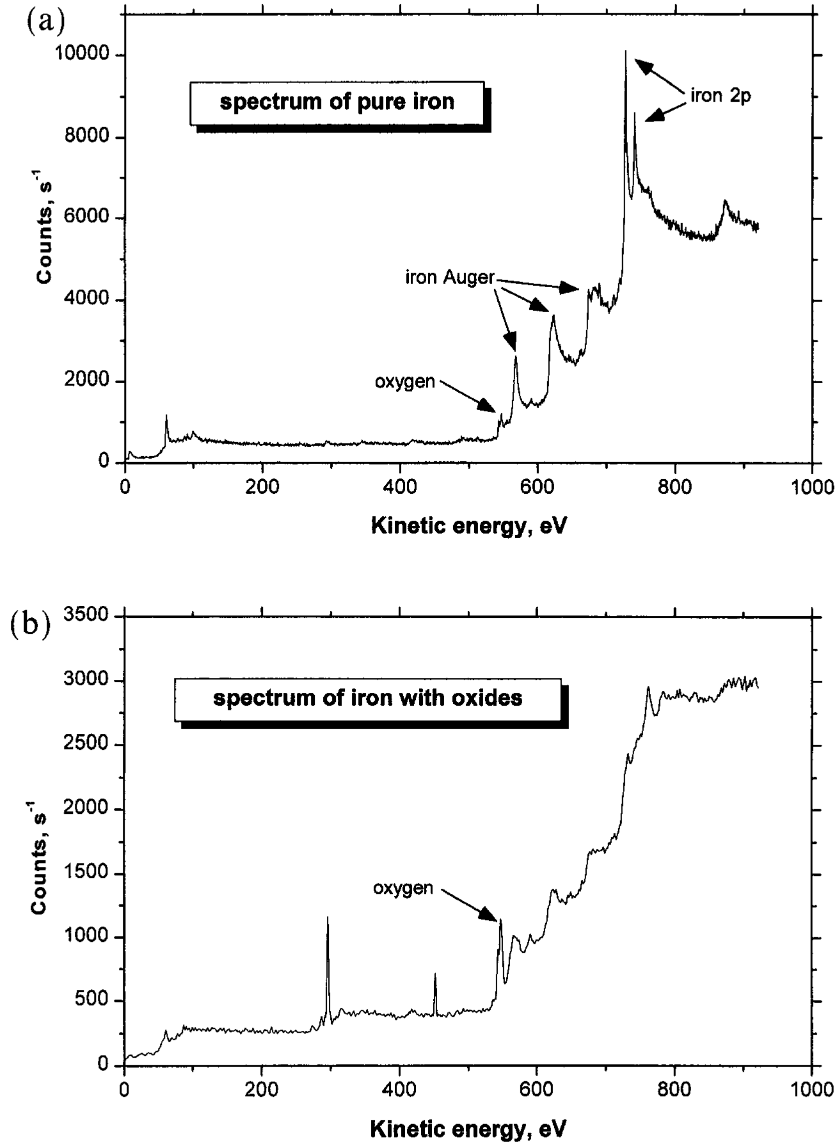

Fig. 8. XPS spectrum of (a) pure iron and (b) iron with oxides.

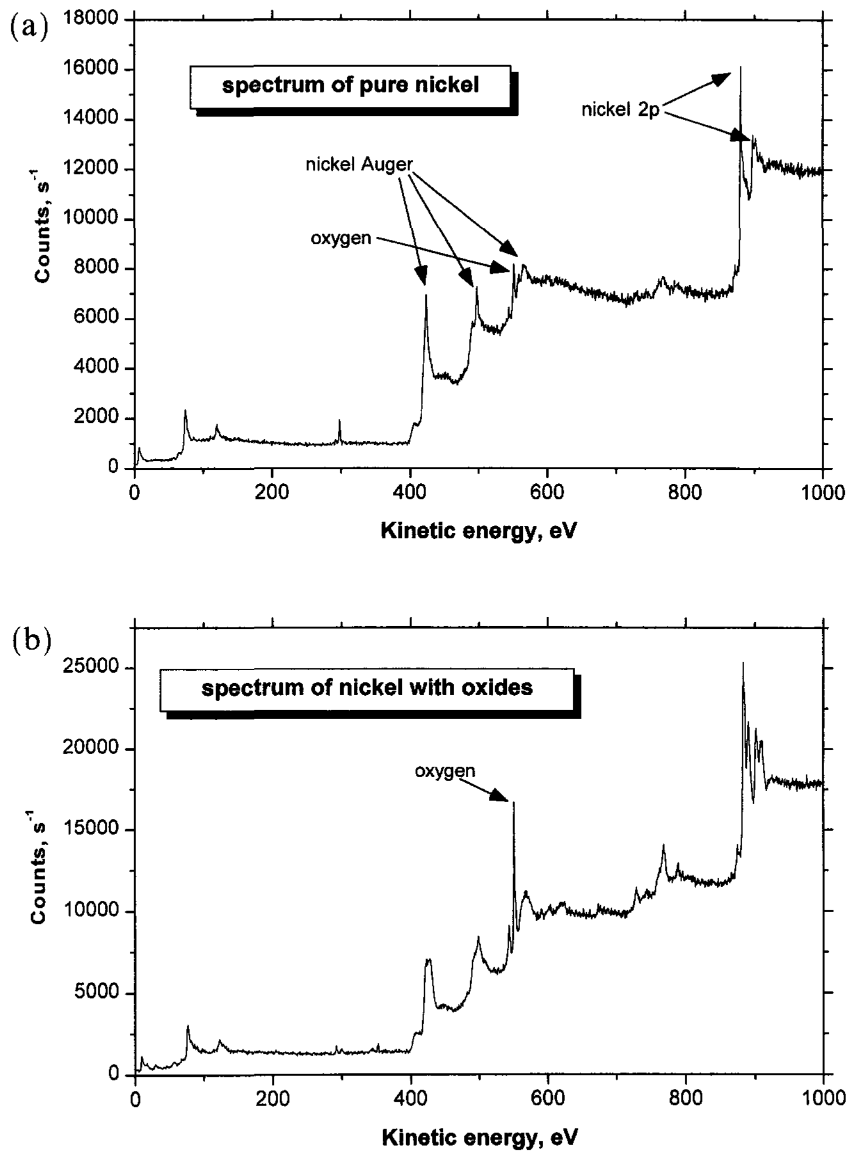

Fig. 9. XPS spectrum of (a) pure nickel and (b) nickel with oxides.

those of Keene [1]. Furthermore, the results of the oxygen measurements show qualitative agreement with the results of Keene [16], Nakashima et al. [17], and Sharan and Cramb [18]. The theoretical analysis of the data is still in progress. Eventually, the effect of oxygen on the binary alloy systems shall be investigated.

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