Note

Ellipsometric Determination of Normal Spectral Emissivities at 632.8 nm for Solid Ni–Co Alloys at High Temperature

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1. Introduction

Normal spectral emissivities of alloys are indispensable to temperature measurements using one-colour pyrometers in various metallurgical processes, because the accuracy in measured temperatures is determined principally by that in emissivity data. In the previous work,¹⁾ one of the present authors reported normal spectral emissivities for solid Cu–Ni alloys at high temperature determined for a wavelength of 632.8 nm by ellipsometry, along with a brief review of emissivity data for solid alloys, which review showed that emissivity data were available only for limited alloys.²⁾ This situation has been unchanged still now and further accumulation of data is required. Thus, the aim of the present work is to determine normal spectral emissivities at 632.8 nm for solid Ni–Co alloys at high temperature by ellipsometry. There is only one report available for emissivity data of the alloy³⁾ although several studies have been made on nickel and cobalt.^{3–8)} Furthermore, emissivity measurements on Ni–Co alloys are of scientific interest because these alloys form complete solid solution in certain temperature ranges, in which the alloys experience magnetic transformation.

2. Experimental

Table 1 gives nominal chemical compositions (in at%) of Ni–Co alloy samples used in the present work. These samples were prepared from grains of Ni and Co with 99.9 mass% purity. Weighed mixtures of Ni and Co grains were placed in alumina crucibles (25 mm in inner diameter) in an induction furnace and then were melted at temperatures above 1 800 K in dehydrated Ar atmosphere for more than 20 min. The melts were slowly cooled down and solidified in the furnace, and the alloys obtained were cut into the shape of a disc (2–4 mm in thickness). The disc samples were homogenised at about 1 473 K in a flow of dehydrated Ar for 2 h and then one face of each sample was polished, finally using alumina abrasives of 0.3 μm in diameter, into mirror-finished surface. Prior to the optical measurement, the samples were rinsed in acetone using an ultrasonic cleaner. Chemical compositions of the samples were determined by X-ray fluorescence analysis, and the analysed

Table 1. Nominal and analysed chemical compositions (in at%) of Ni–Co alloys.

Nominal compositions	Analysed compositions, X_{Co}
Ni-5 %Co	5.6
Ni-20 %Co	22.4
Ni-40 %Co	42.8
Ni-65 %Co	65.6

Fig. 1. Ellipsometer for measuring normal spectral emissivity.

chemical compositions are also given in Table 1.

The normal spectral emissivity for a wavelength of 632.8 nm was determined from the optical constants n and k from the following equation:

$$\varepsilon = \frac{4n}{(n+1)^2 + k^2} \dots\dots\dots (1)$$

The optical constants were in turn measured by an ellipsometer, as shown in **Fig. 1**,^{1,9)} where a He–Ne laser (632.8 nm wavelength and 1 mm beam diameter) was used as the probe light, whose angles of incidence and reflectance were adjusted to 60° with respect to the sample surface. The chamber was filled with dehydrated Ar–10%H₂ to avoid surface oxidation of the samples, and was evacuated to about 0.6 atm during measurements to reduce the fluctuation of the probe light due to gas convection. Measurements were carried out during the heating cycle in the temperature range from room temperature to about 1 600 K at intervals of about 100 K (in some samples, about 25 K around the Curie points), and the temperature of samples was measured with an R-type thermocouple positioned near the sample. More than 30 runs were conducted at each temperature to confirm the reproducibility of the measurements. The pilot experiment confirmed that constant emissivity values could be obtained 15 min after the sample reached a certain temperature, and thus all the measurements were started 20 min after establishment of thermal equilibration.

3. Results and Discussion

Figure 2 shows normal spectral emissivities at 632.8 nm measured on Ni–Co alloys as functions of temperature along with previously reported values,^{1,3,4,6–8)} where the

Fig. 2. Temperature dependence of normal spectral emissivities for Ni–Co alloys for a wavelength of 632.8 nm.

standard deviation of the present experimental data is less than about ± 0.0085 . The emissivity data recorded for Ni in the present work are in agreement with those reported by Tanaka *et al.*,¹⁾ Makino *et al.*,⁴⁾ Gushchin *et al.*⁷⁾ and Burgess and Waltenberg⁸⁾ by less than 10% difference, and the value at 1700 K extrapolated from the present experimental data is greater by about 10% than the value reported by Watanabe *et al.*⁶⁾ The emissivity data for Ni–65.6%Co are also in good agreement with those reported for Ni–65%Co by Wahlin and Knop³⁾ including the complicated behaviour around its Curie point: Wahlin and Knop measured the emissivities using a disappearing filament optical pyrometer and thus the measured wavelength cannot be specified. For Co, the value measured for room temperature in the present work is in very good agreement with the corresponding value reported by Makino *et al.*⁴⁾ However, the measurement could not be made at temperatures higher than its Curie point due to the surface roughness arising from the phase transformation from hcp to fcc structures at 673 K, and the temperature dependence of the emissivity has not been obtained clearly. Furthermore, when samples were oxidised due to improper atmosphere control, emissivity values obtained were approximately twice as large as those shown in the figure. This would suggest that the present measurements were not affected by surface oxidation. In summary, Fig. 2 on the whole shows the following features:

(i) The emissivity values for Ni–Co alloys range be-

Fig. 3. Relationship between emissivities and resistivities for Ni–Co alloys. Solid and open symbols represent data at temperatures lower and higher than the Curie points, respectively.

tween 0.3 and 0.4, irrespective of the alloy composition and temperature, in the range investigated.

(ii) The emissivity values for Ni–Co alloys decrease with increasing temperature up to the respective Curie points and then increase. The magnetic transformation is likely to affect the temperature dependence of the emissivity.

The emissivity of metal is often discussed using the electric resistivity on the basis of the Hagen–Rubens relation¹⁰⁾ given by the following:

$$r = 1 - 4 \sqrt{\frac{\nu}{\sigma_0}} \pi e_0 \dots \dots \dots (2)$$

where r and σ_0 is the reflectivity and dc conductivity of metal, ν is the frequency of light, e_0 is the permittivity of vacuum, and π is the circular constant. Furthermore, there exists the relation $r + t + a = 1$, where t is the transmissivity and a is the absorptivity, and the conditions $\varepsilon = a$ and $t = 0$ apply to metal in thermal equilibrium. As a consequence, the emissivity can be expressed by the following equation:

$$\varepsilon = 4 \sqrt{\rho_0 \nu \pi e_0} \dots \dots \dots (3)$$

where ρ_0 is the dc resistivity of metal, *i.e.*, $\rho_0 = 1/\sigma_0$. Equation (3) means that the emissivity increases in proportion to the square root of the resistivity, which also reflects the mechanism that thermal emission occurs when excited free electrons are relaxed by scattering with phonons. However, it is known that the Hagen–Rubens relation is only valid at wavelengths higher than about $30 \mu\text{m}$ because inner shell electrons more strongly affect the optical process at lower wavelengths. Thus, Eq. (3) does not apply to the emissivity at 632.8 nm strictly but could qualitatively suggest that the emissivity increases as the resistivity increases.

Figure 3 shows the relationship between the emissivities obtained in the present work and the resistivities reported by Ikeda.¹¹⁾ At temperatures lower than the Curie points, the

emissivities decrease with increasing the resistivities, *i.e.*, increasing temperature; on the contrary, at higher temperatures the emissivities increase with increasing the resistivities. Accordingly, the qualitative suggestion from the Hagen–Rubens relation is reasonable in the emissivities at temperatures above the Curie points but is not in the emissivities at temperatures below the Curie points. This finding suggests that inner shell electrons would affect the emissivities of ferromagnetic phases more strongly but the effect would decrease with increasing temperature; however, the mechanism is still uncertain.

Figure 4 shows normal spectral emissivities at 632.8 nm for Ni–Co alloys plotted against the analysed chemical compositions of Co on the basis of Fig. 2. For 300 and 500 K, additions of Co up to about 40% on the whole increase the emissivities but further additions decrease: the values for Ni–22.4%Co exhibit different behaviour, and are shown between parentheses just for information since the reason for the different behaviour is uncertain at the moment. This compositional dependence is qualitatively close to that for the resistivity described by Nordheim’s rule. For

Fig. 4. Emissivities for Ni–Co alloys as functions of Co concentration.

1 000 and 1 500 K, on the contrary, additions of Co decrease the emissivities. Future work should also include explanation for the difference between these compositional dependencies.

4. Conclusions

Normal spectral emissivities of solid Ni–Co alloys have been determined using an ellipsometer for a wavelength of 632.8 nm in the temperature range between room temperature and about 1 600 K. The emissivities range between 0.3 and 0.4 in the range investigated, and decrease with increasing temperature up to the respective Curie points and then increase. Inner shell electrons seem to affect the emissivities of ferromagnetic phases more strongly.

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