Valence Effect in the Electromigration of Impurities in Paramagnetic Nickel

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(Z. Naturforsch. **28 a**, 1492—1495 [1973] ; received 28 March 1973)

The apparent effective charge $\mathbf{Z}^{**}$ of ^{125}Sb, ^{113}Sn, ^{110}Ag, ^{58}Co, ^{59}Fe and ^{54}Mn has been measured in polycristalline paramagnetic nickel, using the thin-layer technique. The atom transport appears to be directed toward the cathode for all the investigated solutes. For left-hand impurities, this effect is interpreted as due to predominant d-hole scattering on the impurity; for right-hand impurities both the direct field effect and d-hole scattering have an influence on the direction of the transport.

Introduction

When a direct electric current is passed through a dilute alloy, the drift velocity of the solute ions is related to the mean force $\mathbf{Z}^{**}\,|e|\,\boldsymbol{\varepsilon}$ acting of them, where $\mathbf{Z}^{**}$ is the apparent effective charge of the solute atoms, $\boldsymbol{\varepsilon}$ is the electric field and $|e|$ is the absolute charge of the electron.

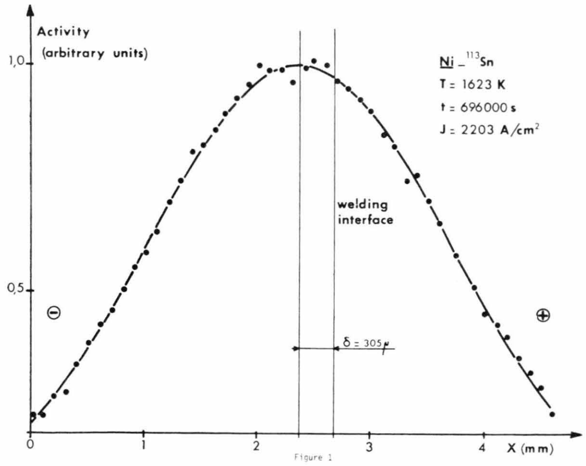

Fig. 1. Typical concentration profile obtained with the thin-layer technique.

This paper reports the results of measurements of $\mathbf{Z}^{**}$ in paramagnetic nickel for the following impurities: ^{125}Sb, ^{113}Sn, ^{110}Ag, ^{58}Co, ^{59}Fe and ^{54}Mn, using the thin-layer technique [1, 2].

In this technique, $\mathbf{Z}^{**}$ is deduced from the shift δ of the maximum of the concentration profile from the original welding interface as shown in Figure 1.

$$\mathbf{Z}^{**} = \delta k T / D^{*} t\,|e|\,\varrho_0 J \tag{1}$$

where D^{*} is the correlated diffusion coefficient of the solute atoms, ϱ_0 is the host resistivity at the temperature T of the experiment, t is the diffusion time and J is the current density. The $D^{*}\,t$ product involved in Eq. (1) is directly deduced from the shape of the gaussian activity profile, the temperature being measured with an optical pyrometer. When the temperature dependence of D^{*} is known, this measurement of $D^{*}\,t$ provides a check of the estimation of the temperature.

The $D^{*}\,t$ product is corrected for the welding time according to the usual relation:

$$D^{*}\,t = 1/4\,p - D_{\mathrm{s}}\,t_{\mathrm{s}} \tag{2}$$

where p is the slope of the curve $\ln c = f[(x - x_{\mathrm{m}})^2]$, c is the impurity concentration, D_{s} and t_{s} are respectively the diffusion coefficient at the welding temperature and the duration time of the welding; x_{m}, the position of the maximum, is obtained through a least mean square deviation fit of the experimental data to the linear relation $\ln c = f[(x - x_{\mathrm{m}})^2]$, as shown in Figure 2.

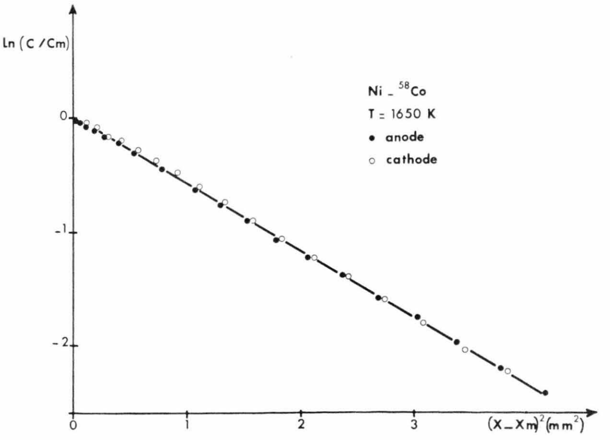

Fig. 2. Ln (specific activity) versus the square of $x - x_{\mathrm{m}}$ (distance from the maximum).

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Experimental Results

In the present electromigration experiments measurements of $\boldsymbol{Z}^{**}$ have been performed in high purity polycristalline nickel (5 N). As the maximum concentration of the tracer reduces to less than 100 ppm in the first hour of the runs, it is reasonable to use in (1) the resistivity ϱ_0 of pure nickel, given in this temperature range by [3].

$$\varrho_0(T)\,(\mu\Omega\cdot\text{cm}) = 19.1 + 2.25 \times 10^{-2}\,T\,. \quad (3)$$

In the determination of the current density J, the thermal expansion of the sample is accounted for using the linear thermal expansion coefficient [4]:

$$\beta(T) = 1.28 \times 10^{-5} + 0.5 \times 10^{-8}\,T\,. \quad (4)$$

Some values of $\boldsymbol{Z}^{**}$ obtained in this way are listed in Table 1. These values of $\boldsymbol{Z}^{**}$ are plotted as a function of $A' - A$, the difference between A', the atomic number of the solute and A, the atomic number of the solvent (Fig. 3), together with the value obtained by Wever [5] for the self-diffusion of Ni. Doan [6] has shown that the apparent effective charge of the solute must be corrected for "vacancy flow effects" in order to obtain the true effective charge $\boldsymbol{Z}^*$ of the impurity. The formula giving $\boldsymbol{Z}^*$ as a function of $\boldsymbol{Z}^{**}$ is:

$$\boldsymbol{Z}^* = \boldsymbol{Z}^{**} + \alpha\,\boldsymbol{Z}_{\text{Ni}}{}^*\,. \quad (5)$$

Clearly, the vacancy flow effects arise from the fact that the solvent atoms are submitted to a force from the electric field. The coefficient α involves some ratios of vacancy jump frequencies around the impurity which are not known accurately in nickel alloys. Then, the true effective charge $\boldsymbol{Z}^*$ cannot be deduced from the present measurements. Actually, Doan [7] has shown that some information about these ratios could be obtained from self-diffusion and impurity diffusion electromigration experiments. Unfortunately, such experiments lack at the present time although, together with standard electromigration experiments, they would allow a deeper insight in the analysis of the electronic structure of the moving ion.

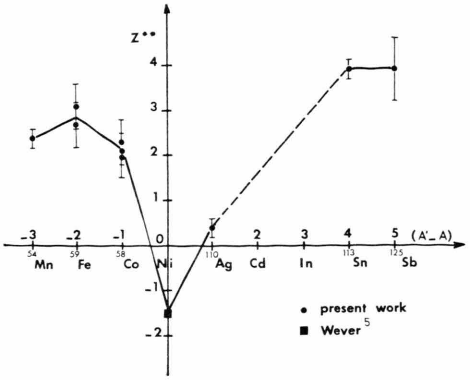

Fig. 3. Apparent effective charge $\boldsymbol{Z}^{**}$ as a function of $(A'-A)$, the difference between the atomic numbers of the solute and the solvent.

Discussion of the Experimental Data

1. Direct electrostatic force

According to Bosvieux and Friedel [8], the total electrostatic force on the impurity ion in a normal metal is the sum of the force $Z'|e|\boldsymbol{\varepsilon}$ on the ion itself and of $-(Z'-Z)|e|\boldsymbol{\varepsilon}$, the force on the screening charge, where Z is the charge of the solvent ion (the number of conduction electrons per atom), and $(Z'-Z)$ the relative charge of the solute ion with respect to the solvent.

The force acting on the screen is transmitted to the ion, as if the screening charge were tightly bound to the impurity ion.

Table 1. Apparent effective valence of ^{125}Sb, ^{113}Sn, ^{110}Ag, ^{58}Co, ^{59}Fe, ^{54}Mn in paramagnetic Ni host.

T (K)	t (10^5 s)	J (A/cm^2)	δ (μm)	$\boldsymbol{Z}^{**}{}_{^{125}\text{Sb}}$	$\boldsymbol{Z}^{**}{}_{^{113}\text{Sn}}$	$\boldsymbol{Z}^{**}{}_{^{110}\text{Ag}}$	$\boldsymbol{Z}^{**}{}_{^{58}\text{Co}}$	$\boldsymbol{Z}^{**}{}_{^{59}\text{Fe}}$	$\boldsymbol{Z}^{**}{}_{^{54}\text{Mn}}$
1630	3.89	2488	242	$+3.9 \pm 0.7$					
1650	6.05	2253	413		$+3.9 \pm 0.2$				
1623	6.96	2203	305		$+3.9 \pm 0.2$				
1632	7.76	2365	25			$+0.4 \pm 0.2$			
1650	15.50	2208	77				$+2 \pm 0.5$		
1650	7.42	2316	64				$+2.3 \pm 0.5$		
1637	13.80	2098	59				$+2.1 \pm 0.5$		
1630	12.90	2126	459					$+3.1 \pm 0.5$	
1630	12.75	2274	521					$+2.7 \pm 0.5$	
1650	6.07	2100	236						$+2.4 \pm 0.2$

This approximation is clearly valid in a free-electron model as the screen follows instantaneously the ion in the course of its diffusion jump.

In a transition metal however, the screening occurs mainly in the d-band, owing to the large density of d-states at the FERMI level. In addition to local field effects arising from the polarisation of d-orbitals, the screening and therefore the nature of the force acting on the impurity ion are different according as the valence of the impurity is smaller or larger than that of the host metal:

a) In the case of impurities of smaller valence than the solvent, the screening charge is almost completely localized on the impurity site [9]. The diffusing particle is then the ion surrounded by its complete d-screen and the total electrostatic force is:

$$\boldsymbol{F}_\varepsilon = c_s \, |e| \, \boldsymbol{\varepsilon}$$

where c_s is the number of s-electrons per atom of the solvent. This force is essentially of the same nature as in the case of a free electron model.

b) For impurities whose relative valence with respect to the solvent is small and positive, the same behaviour is to be expected because there is a sufficient number of empty states in the d-band to allow a complete or almost complete screening on the impurity site.

c) For impurities of larger valence however, a small fraction of the screening occurs on the impurity site and the extra charge of the impurity ion is screened by electrons in d-atomic orbitals of neighboring ions. It is not clear in this case to what extent the electrostatic force acting on screening electrons attached to neighboring ions is transmitted to the jumping impurity. Actually, the neighbors themselves are also acted by this force and a part of it is transmitted to the impurity through elastic atom-atom interactions. Then, this direct electrostatic force on the impurity may be written:

$$\boldsymbol{F}_\varepsilon = \mathbf{Z}' \, |e| \, \boldsymbol{\varepsilon} + \gamma (\mathbf{Z} - \mathbf{Z}') \, |e| \, \boldsymbol{\varepsilon}$$

where γ is essentially the fraction of the total number of screening electrons attached to the impurity ion itself.

2. *Scattering of* **s** *and* **d** *carriers*

The scattering of **s** and **d** carriers on the impurity leads to a force which is calculated in this section. We define the specific **s** (**d**) resistivity $\varrho_s{}^i (\varrho_d{}^i)$ of the impurity such that $\varrho_s{}^i c_i \, (\varrho_d{}^i c_i)$ represents the residual **s** (**d**) resistivity of an atomic concentration c_i of impurities:

$$\varrho_s{}^i c_i = \frac{|m_s{}^*|}{n_s e^2 \tau_s{}^i} \; ; \quad \varrho_d{}^i c_i = \frac{|m_d{}^*|}{n_d e^2 \tau_d{}^i} \tag{6}$$

where n_s and n_d are respectively the density of **s** and **d** conduction carriers, whose effective masses are $m_s{}^*$ and $m_d{}^*$. In the definition of the relaxation times $\tau_s{}^i$ and $\tau_d{}^i$, four possible channels for the scattering are considered: although the **s** resistivity arises mainly from **s**-**d** transitions, we may define a relaxation time $\tau_s{}^i$ in the **s** band [10] as a function of $\tau_{ss}{}^i$ and $\tau_{sd}{}^i$ the relaxation times for **s**-**s** and **s**-**d** scattering respectively:

$$1/\tau_s{}^i = 1/\tau_{ss}{}^i + 1/\tau_{sd}{}^i \, . \tag{7}$$

The scattering relaxation time of the impurity in the **d**-band is defined in the same way:

$$1/\tau_d{}^i = 1/\tau_{dd}{}^i + 1/\tau_{ds}{}^i \, . \tag{8}$$

Using the formalism given by Huntington [11] and Fiks [12], we then calculate the total force $n_i \vec{\boldsymbol{F}}$ due to the scattering of the carriers on the n_i impurities embedded in a unit volume of the dilute alloy:

$$n_i \, \boldsymbol{F} = - \frac{1}{|e|} \left[\boldsymbol{J}_s \left(\frac{m_s{}^*}{\tau_s{}^i} \right) + \boldsymbol{J}_d \left(\frac{m_d{}^*}{\tau_d{}^i} \right) \right] \tag{9}$$

where $\boldsymbol{J}_s$ and $\boldsymbol{J}_d$ are the current densities in the **s** and **d** bands respectively. Defining $j_s = J_s/J$ and $j_d = J_d/J$, the fractions of current contributed by each band, c_s and c_d the number of atomic **s** and **d** conduction electrons, it is straightforward to obtain the effective charge $\mathbf{Z}_{sc}{}^*$ due to the scattering of **s** and **d** carriers on the impurity:

$$\mathbf{Z}_{sc}{}^* = - \frac{1}{\varrho_0} \left[j_s \, c_s \, \varrho_s{}^i \frac{m_s{}^*}{|m_s{}^*|} + j_d \, c_d \, \varrho_d{}^i \frac{m_d{}^*}{|m_d{}^*|} \right] \tag{10}$$

where ϱ_0 is the lattice resistivity of the alloy. Therefore, even in the presence of **s**-**d** and **d**-**s** scattering the effective charge $\mathbf{Z}_{sc}{}^*$ can be separated in two independent **s** and **d** parts.

The **s** part of $\mathbf{Z}_{sc}{}^*$ is negative but the **d** part is positive, $m_d{}^*$ being negative for a nearly filled **d** band. $\mathbf{Z}_{sc}{}^*$ is then the result of two opposite contributions. It is well-known that in nickel j_s is much greater than j_d because of the high effective mass of *d* holes, but c_s is much smaller than c_d owing to the large density of states in the **d** band and the **d** part may dominate the **s** part depending on the value of $\varrho_d{}^i / \varrho_s{}^i$.

A detailed analysis of $\mathbf{Z}_{\mathrm{sc}}{}^*$ is currently in progress following the work of Gomes [13]. Furthermore measurements of the specific resistivity of transition impurities in paramagnetic nickel are planed to get complementary informations on the scattering of electrons by impurities.

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