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EFFECT OF MAGNESIUM ADDITION ON THE VACANCY-Mg BINDING FREE ENTHALPY IN Al-Cr ALLOYS

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ABSTRACT: The Mg-vacancy binding free enthalpy of Al-Cr solid solution alloys with Mg addition was calculated by electrical resistivity measurements. The obtained value is lower than that obtained for dilute Al-Mg alloys with almost the same Mg content and may be attributed to the diffusion of Mg.

KEYWORDS: Electrical properties; resistivity; vacancy; binding free enthalpy.

Introduction

Previous works show that there is a considerable variation on the magnitude of the experimental values of the vacancy-impurity binding enthalpy in binary alloys, obtained with the application of different techniques (specific heat, positron annihilation, comparing the length change and lattice parameter change, residual resistivity, solvent enhancement of diffusion at equilibrium temperature) and specifically of the vacancy-magnesium binding enthalpy g in the dilute Al-Mg alloy[18,12,5,10,19,8].

Theoretical estimations, based on the screening potential method[9], on the pseudopotential method[16], on the second-order perturbation theory[17], on the cohesive energies of pure Al and pure Mg and the heat of solution of the solution atoms[7], are generally in fairly poor agreement with experimental data.

From the harmonic model[11],

$$R \approx T(\theta_B)^{-2} \qquad (1)$$

where R is the electrical resistance of the metal, T is the absolute temperature and q_B is the Debye temperature. From thermodynamics[14] one gets

$$\frac{d \ln (R/T)}{dT} = 2\alpha\gamma \qquad (2)$$

where a(T) is the volumetric thermal dilatation coefficient of the metal and g(T) is the Grüneisen parameter. It is experimentally verified that the linear relationship of equation (2) has no physical meaning for determined values of a(T) and g(T), because of their substantial anharmonic contributions[12].

The measurement of the equilibrium impurity-vacancy binding enthalpy in metals from electrical resistivity, by its great sensibility, is one of the best, despite the weak theoretical justification of the criterion for low-to-high temperature extrapolation of the lattice resistivity. This was overcome by an empirical method based on the fact that the plot of experimental ln(R/T) data versus T, figure 1, is linear up from a specific to a high enough temperature to allow extrapolation of the lattice resistivity[3,1]. The slight upward deviation of the curve, in that figure, is attributed to the increasing thermal equilibrium vacancy formation.

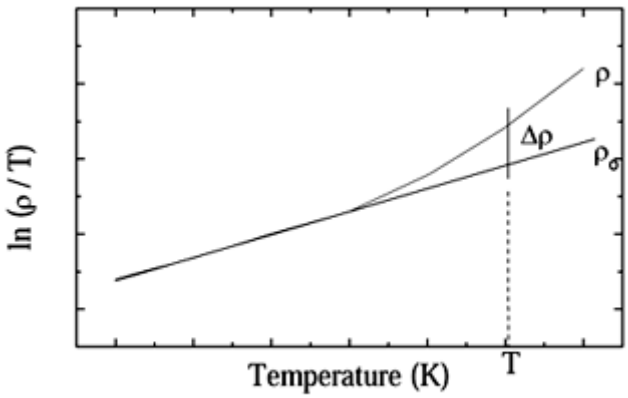

Figure 1 - Schematic diagram of ln (ρ/T) versus T

The electrical resistivities r and r_0, Fig.1, are respectively proportional to

$$\rho = k(n_A + n_B + n_V) \qquad (3)$$

and to

$$\rho_0 = k(n_A + n_B) \qquad (4)$$

where n_A, n_B are, respectively, the number of lattice positions of A and B atoms and n_V is the total number of vacancies, and k is the coefficient of proportionality (W × cm). For

$$\frac{\Delta\rho}{\rho_0} = \frac{[k(n_A + n_B + n_V) - k(n_A + n_B)]}{k(n_A + n_B)} \qquad (5)$$

results

$$\frac{n_V}{n_S} = \frac{n_V}{n_A + n_B} = \frac{\Delta\rho}{\rho_0} \qquad (6)$$

The statistical analysis for the determination of thermal equilibrium vacancy concentration in a diluted binary A-B alloy, being A the metal solvent and B the dilute or impure metal, with arbitrary concentration[15,20], considers the existence of a positive binding free enthalpy between vacancies and impurity atoms. According to Dorn-Mitchell[6], the equilibrium concentration of a substitutional regular solid solution of A and B atoms is given by

$$\frac{n_V}{n_S} = \sum_{i=0}^{Z} \frac{n_i}{n_S} \cong \sum_{i=0}^{Z} \left| \frac{Z}{i} \right| X_B^i X_A^{Z-i} \exp(-g_i/kT) \qquad (7)$$

where n_i is the number of vacancies coordinated with i atoms B and (z-i) atoms A, 0 £ i £ z, n_s = n_A+n_B+n_V is the total number of lattice positions, n_v is the total number of vacancies and n_A and n_B are the numbers of A and B atoms in the alloy, X_A and X_B are the solvent and solute atomic fractions and g_i the free enthalpy of formation between a vacancy and i solute atoms, which depends only on the atoms coordinated with a vacancy.

For i = 0 the right hand term of expression (7) for $(X_A)^{12}$ @ 1 becomes exp ($-g_0/kT$), indicating the absence of a vacancy-B atoms binding free enthalpy.The normalization of the Dorn-Mitchell's expression with exp($-g_0/kT$) becomes equivalent to n_V/ n_S=Dr /r_0 .

According to the Matthiessen's rule,

$$\rho = \rho_i + \rho_0 + \Delta\rho \qquad (8)$$

where r_i is the impurity (solute) electrical resistivity, which is nearly independent of the temperature, r_0 is the electrical resistivity given by the matrix lattice vibration, which depends on the temperature and r is the electrical resistivity change caused by the thermal equilibrium vacancies, which concentration grows exponentially with the temperature.

Taking equation (6), where r and r_0 are obtained, respectively, from the anti-ln(r /*T*) and anti-ln(r_0/*T*) of the ascendant part and at the extended rectilinear part of the curve, at the same temperatures (Fig. 1), it is possible to measure the concentration of thermal vacancies on heating[2-1].

Because the lack of a expression for a ternary alloy, as did Dorn-Mitchell for binary alloys, we just experimentally investigated the r /r_0 behavior with Mg composition of the Al-Cr-Mg alloy.

Experimental Procedure

The studied alloys were prepared by ALCAN-CANADA, with compositions showed on Table I.

Table I - Chemical composition (weight % / atomic %) of the studied alloys

Alloy	Element		
	Al	Mg	Cr
1	99.959/99.979	-	0.041/0.021
2	99.717/99.710	0.245/0.270	0.039/0.020
3	99.605/99.598	0.349/0.387	0.046/0.024
4	99.462/99.434	0.488/0.541	0.048/0.025
5	99.319/99.278	0.625/0.693	0.056/0.029

Wires of the alloys, with 0.05 cm diameter, were obtained by cold-rolling. The specimen were screw-shaped, fixed on a ceramic holder and annealed in argon atmosphere. The potentiometer contacts were made by wires of the same alloy. A K-3 Leeds & Northrup potentiometer, a Cambridge galvanometer with 50 ohm internal resistance and a tubular furnace with controlled temperature were used for equilibrium temperature electrical resistivity measurements in controlled atmosphere. A constant electrical current of 200 mA was controlled by using a standard resistance at constant temperature.

Results and Discussion

Figure 2 shows the plot of residual electrical resistivity Dr/r_0, designated by Dr_N, vs. Mg composition, obtained according to the method presented in Fig.1, where the Al-Mg[19] and the Al-Cr-Mg curves are normalized to their respective extended rectilinear parts of the curve at 855 K, from the experimental range 400K-860K.

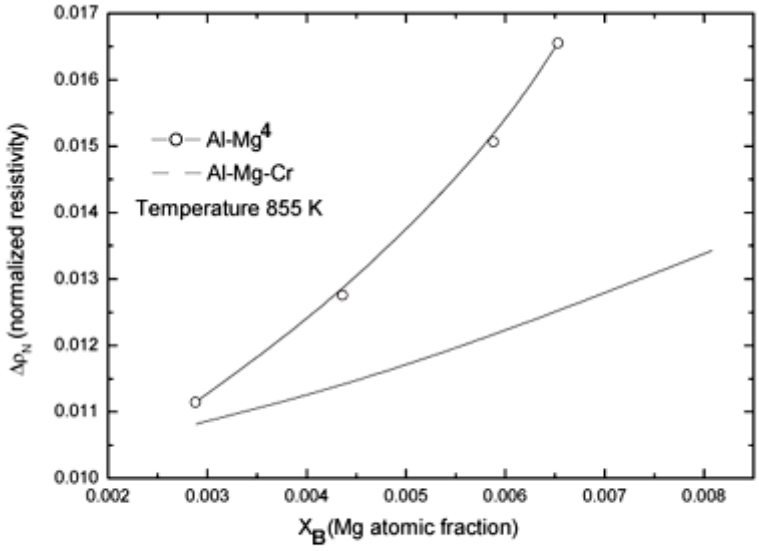

Figure 2 - Normalized resistivity changes ($\Delta\rho_N$) versus magnesium composition (X_B).

From Fig. 2 it is possible to see that the thermal vacancies contribution is lower than that obtained for Al-Mg alloys with same Mg content[4,13].

Conclusions

The thermal equilibrium method here adopted shows an increase of Dr_N with the Mg concentration and that thermal vacancies contribution must be modified by the Mg addition.

When we compare the Dr_N of the Al-Mg and of the Al-Cr-Mg alloys behavior, the dilute element Cr seems to low significantly the total number of vacancies linked with different numbers of Mg atoms.

Because the low concentration of Cr in the Al-Cr-Mg, alloy the influence on the Dr_N values by the residual resistance, caused by the maximum scattering of the Fermi electrons[9] at the experimental range 400K-860K, is small.

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BEATRICE, C. R. S., GARLIPP, W., CILENSE, M., ADORNO, A. T. Efeito da adição de magnésio na entalpia livre de ligação vacância-Mg em ligas de Al-Cr. *Ecl. Quím. (São Paulo),* v.27, p. , 2002.

RESUMO: *A entalpia livre de ligação vacância-Mg, em ligas com solução sólida de Al-Cr contendo adição de Mg, foi calculada por medidas de resisitivadade elétrica. O valor obtido foi*

menor do que aquele obtido para ligas diluídas de Al-Mg com aproximadamente a mesma concentração de Mg e pode ser atribuído à difusão do Mg.
PAVRAS-CHAVE: *propriedades elétricas; resisitividade; vacância; entalpia livre de ligação.*

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