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A Model of Vacancy Flux Induced Segregation to Grain-Boundaries During Cooling

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A recently developed method of analysis provided a direct measure of grain-boundary solute enrichment in slowly cooled Zn-Cd alloys as a function of holding temperature. These experimental data are here compared with the change of boundary solute enrichment computed from a model based on the vacancy flux generated uphill diffusion of solute to boundaries. The agreement between experiment and theory is satisfactory. This agreement is considered to be a direct proof that previously reported grain-boundary hardening of slowly cooled dilute alloys is a consequence of non-equilibrium solute adsorption.

1. Introduction

Recently it was shown [1, 2] that in certain alloy systems grain-boundary regions become harder than the bulk of grains when the alloys are cooled from an elevated holding temperature. Aust *et al* [2] have attributed this grain-boundary hardening to solute clusters resulting from the decomposition of solute-vacancy complexes in the vicinity of the boundary (vacancy sink). This concept was supported by the observation that for alloys in which an attractive interaction between solute atoms and vacancies could be expected, boundary hardening occurred. Conversely, in pure material and alloys whose solute was expected to have a repulsive interaction with vacancies, boundary softening occurred after cooling from elevated temperatures. The sign and magnitude of the vacancy-solute interaction energy would thus dictate how much solute would be transported to grain-boundaries during cooling at a given rate from a certain holding temperature.

In an attempt to test this model of solute transport, the present authors have recently developed a method for a direct analysis of the grain-boundary solute concentration [3]. This analysis enabled them to detect whether or not boundaries were solute enriched and relate this enrichment to Aust *et al*'s grain-boundary hardness results. For a dilute zinc-cadmium alloy, it was possible to obtain quantitative measurements of the difference in solute concentration between boundary regions and the bulk of grains as a function of holding temperatures and cooling rates. This data can be used to test the validity of the uphill solute diffusion mechanism suggested by Aust *et al.* Therefore, in this work a model has been developed which can predict the variation of non-equilibrium solute adsorption with holding temperature. The results obtained from this model are compared with the experimental measurements.

2. Experimental

The experimental procedure has been described previously [3]. It will be summarised here. Polycrystalline samples of nominal Zn–0.1 at. % Cd alloys were held at different elevated temperatures and cooled to room temperature under a constant cooling rate of 0.05° C $\sec^{-1}$. After the chemical removal of a surface layer, the samples were given a chromatising treatment which rendered their surface resistant to attack by dilute nitric acid, except at the grain-boundaries. Grain-boundary regions of constant width and depth could, therefore, be removed by etching in a solution of nitric acid and this solution was analysed for cadmium and zinc by

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atomic adsorption spectrophotometry. To obtain a measure of the solute concentration difference between boundary regions and bulk grains, the same spectrophotometric method was employed using the etching solutions from the corresponding unprotected specimens.

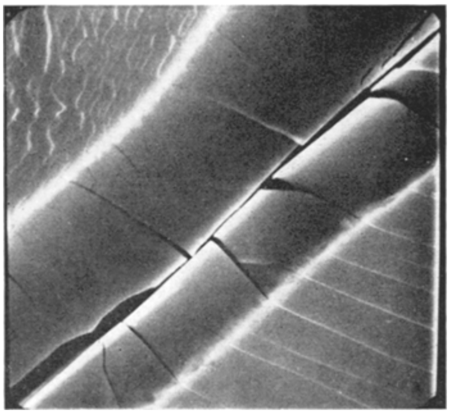

Figure 1 Showing protective layer having collapsed into the trough formed by dissolution of the sample at the grain-boundary-surface intersection (× 4850).

A representation of an etched boundary is given in fig. 1. The etching solution penetrated into the alloy at the poorly protected line of the surface-boundary intersection, dissolving a region approximately 7 μm wide from below the protective layer which collapsed into the boundary trough.

The results are summarised in table I.

3. Mathematical Model

The formation of vacancy-solute complexes may be presented by the reaction

$$V + I \rightleftharpoons C \tag{1}$$

where V, I and C are the concentrations (atomic fractions) of free vacancies, unbound solute atoms and vacancy-solute complexes respectively.

According to Cotterill [4], and Damask and Dienes [5] who found that in the range of solute concentrations used in this work, C/V remained constant during the decay of a quench-induced supersaturation of vacancies, it is readily shown that at all temperatures

$$\frac{C}{V} = K' \exp\left(\frac{B}{\mathrm{R}T}\right) \tag{2}$$

where B is the vacancy-solute binding energy. If the equilibrium concentration of free vacancies, V, is expressed by the usual Arrhenius law with E_F being the formation energy, the equilibrium concentration of complexes in the grains, C_G, is then given by

$$C_\mathrm{G} = K \exp\left(\frac{-E_\mathrm{F} + B}{\mathrm{R}T}\right) . \tag{3}$$

The temperature-independent constant K would include the entropy of complex formation.

According to the segregation mechanism proposed by Aust *et al*, a vacancy concentration gradient develops near a grain-boundary during cooling. The vacancies within the diffusive range, i.e. those experiencing this vacancy gradient, will diffuse toward the boundary. Because of the attractive interaction between cadmium atoms and vacancies in zinc, there will also be a net transport of cadmium atoms toward the boundary. Therefore, the number of excess solute atoms present in the 7 μm wide grain-boundary etching trough should be equal to the number of diffusing vacancy-solute complexes which can reach this trough during cooling. The basic assumption in this work is that the measured solute excess of the dissolved boundary troughs is proportional to the total solute diffused to boundary regions.

Furthermore, we adopt the generally accepted concept of a grain-boundary being an infinite sink for vacancies, such that at all times during cooling the concentration of vacancies at the boundary is zero. According to equation 2, the concentration of complexes at the boundary is therefore also zero.

As the boundary solute build-up increases, it

TABLE I

Holding temp, °C	Holding time, min	Bulk conc, at. %	Grain bdy conc, at. %	% change between bulk bdy and bulk concentration
380	15	0.080	0.140	75
320	45	0.100	0.156	56
275	90	0.096	0.128	33.5
260	120	0.113	0.147	30
250	150	0.096	0.124	29
200	150	0.096	0.111	16

interferes with diffusing complexes and prevents them from diffusing freely to the grain-boundary. This may be represented as a decrease in the efficiency of the *source* of complexes. This loss of efficiency is proportional to the grain-boundary solute enrichment. This decrease may thus be represented by a decrease of the equilibrium concentration of complexes in the grains so that the *effective* bulk concentration at any time during cooling is $C_G - G_B$ instead of C_G given by equation 3.

According to the foregoing, at any temperature, the rate of change of the term C_B can be represented by

$$\frac{dC_B}{dt} = k\,(C_G - C_B)\,, \tag{4}$$

because the rate of grain-boundary solute enrichment is proportional to the effective bulk concentration $C_G - C_B$.

In the absence of any information about the mechanism of the blocking effect we shall consider k to be temperature-independent. This assumption will constitute a basis for further discussion of the mechanism.

For the cooling rates employed, temperature, T, and time, t, are related during cooling by the linear relationship

$$T = T_0 - at \tag{5}$$

where T_0 is the holding temperature and a, the rate of cooling, was 0.05° C sec^{-1}. From equations 3, 4 and 5 C_B can be expressed by the first order differential equation

$$\frac{dC_B}{dt} + kC_B = k \exp\left[\frac{-E_F + B}{R(T_0 - at)}\right]$$

and for the boundary condition $C_B = 0$ at $t = 0$, the solution for $C_B(t)$ is

$$C_B(t) = e^{-kt} \int_0^{t_1} k \exp\left[\frac{-E_F + B}{R(T_0 - at)} + kt\right] dt\,. \tag{6}$$

According to the model, the diffusion profile at temperature T_1 at time t, is given by line I in fig. 2.

The diffusion distance x_{t_1} is given by

$$\frac{x_{t_1}}{2} = \sqrt{\int_0^{t_1} D(t)\,dt}$$

and the diffusion coefficient $D(t)$ is

$$D(t) = D_0 \exp\left(\frac{-E_M}{RT}\right)$$
$$= D_0 \exp\left[\frac{-E_M}{R(T_0 - at)}\right] \tag{7}$$

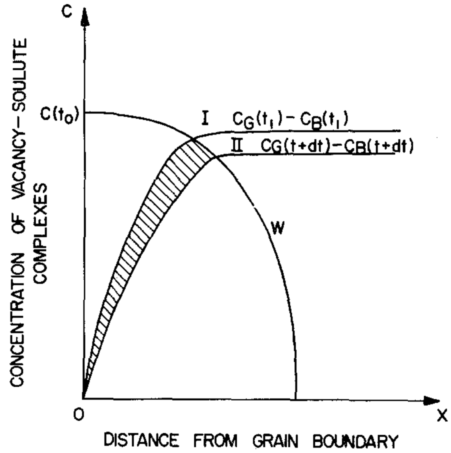

Figure 2 Schematic representation of the diffusion model at two different times during cooling.

where E_M is the activation energy for vacancy migration and D_0, the diffusion constant.

At a time $t_1 + dt$, the diffusion profile is given by line II in fig. 2. Within the diffusion distance, all the complexes annihilated during time dt have migrated to the boundary. This number of complexes is represented by the shaded area in fig. 2.

For the whole cooling process, the number of complexes which have migrated to the boundary is represented by the area located under the curve W. Considering that at room temperature the number of vacancies is negligible, this area is equal to

$$\int_0^{t_F} x(t)\,d\,(C_G - C_B)$$

where $t_F = (T_0 - 293)/a$. Therefore, if N_c is the calculated number of complexes which have reached 1 cm^2 of the grain-boundary,

$$N_c = \int_0^{t_F} x(t)\,(dC_G - dC_B) \tag{8}$$

with

$$dC_G = \frac{a}{R(T_0 - at)^2}\,(E_F - B) \exp \left[\frac{-E_F + B}{R(T_0 - at)}\right] dt$$

and dC_B is given by equation 6. Because K and D_0 are only multiplicative factors (K in dC_G and D_0 in $x(t)$), both will be taken as equal to unity.

4. Results

If the present model is correct, then N_c, calculated for different holding temperatures, should be proportional to the solute excess, N_m, found experimentally for the corresponding holding temperatures.

N_c has been computed using an IBM 360/75 computer. For this, it was necessary to ascribe numerical values to the different energies involved. To evaluate the activation energies for the formation and migration of vacancies, the usual approximation was used

$$E_D = E_F + E_M$$

where E_D is the activation energy for self-diffusion in zinc. The value assigned to E_D was 21.8 kcal/g at. [6]. Many determinations of the formation energies of vacancies in a number of metals, including zinc, by Gertsriken and Slyusan [7] have shown that $(E_F/E_D) = 0.3$ to 0.4. If for this ratio an average value of 0.35 is used, E_F is about 7.7 kcal/g at. and $E_M = 14.1$ kcal/g at. B was taken as 1000 cal/g at. [7].

Of course, the factor k in equation 4 is not known. A value of $k = 0.022$ was found to give the best results. This value is totally arbitrary because of the former stipulation that $K = 1$ and $D_0 = 1$.

The results of these calculations are presented in fig. 3 where N_c, expressed in arbitrary concentration units, is plotted against the measured grain-boundary solute excess for a series of holding temperatures. It is seen that, except for the lowest temperatures, N_c and N_m are proportional.

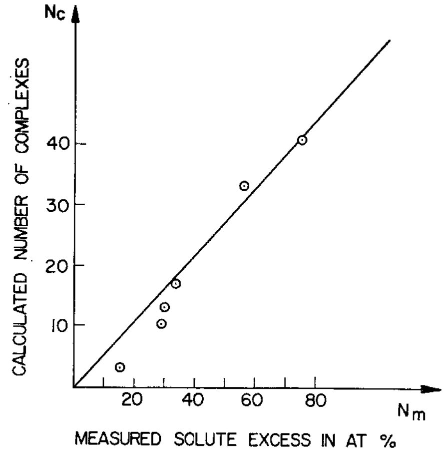

Figure 3 Plot of the calculated number of complexes eliminated at the boundary, in arbitrary concentration units, versus the measured boundary solute excess.

5. Discussion

The above proportionality between the calculated and measured boundary solute excess sustains the concept of an uphill solute diffusion process due to the migration of vacancies to grain-boundaries during cooling.

Another indication of the validity of the present model was provided by calculating N_c for different cooling rates. It was found that N_c was only very weakly dependent on cooling rate until extremely high values were assigned to the cooling rate. This is in accord with previously published results [3] which showed that the measured boundary solute excess was independent of cooling rates except when samples were quenched from holding temperatures into brine.

The assumption made in equation 4 that k is temperature-independent provided good agreement with the experimental results. To rationalise this it is necessary to consider the nature of this constant. As written in equation 4, k appears to be the rate constant of a first order reaction, and should therefore be strongly temperature-dependent. However, considering that the temperature-dependence of diffusion and vacancy and complex concentrations are contained in C_B and C_G, k appears to be a parameter which is directly related to the segregation mechanism at the boundary. To explain the temperature-independence of k a further consideration of the segregation mechanism is in order.

Aust *et al* [2] have proposed that near the grain-boundary, collisions between vacancy-solute complexes become increasingly frequent. These collisions can release one or more vacancies which migrate to the sink, leaving behind a less mobile cluster of solute atoms which may or may not also have a vacancy attached. Subsequent encounters with other vacancy-solute pairs can lead to growth of these solute clusters. It is possible that the vacancies which are trapped together with the solute atoms in such clusters contribute to the formation of dislocation loops around them. These loops would then release the elastic distortion created by the clusters and would allow them to grow. The solute clusters are more stable at low temperatures, and they will be bigger and more numerous as the boundary is approached and as cooling proceeds.

In any case, if such clusters are responsible for the grain-boundary hardening observed by previous workers, they must be present over a distance of 40 to 50 μm from the boundary,

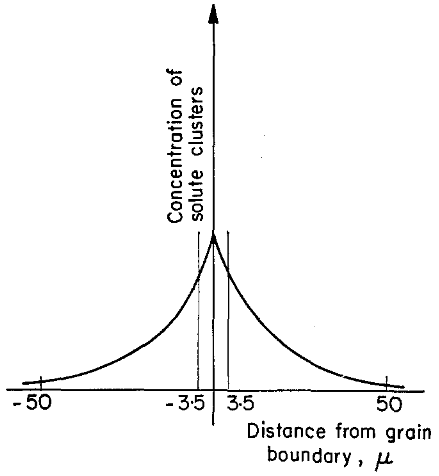

Figure 4 Relation of extent of grain-boundary hardening [2] attributed to solute clusters to the width of the analysed region in this work.

which is much wider than the 3.5 μm etched on each side of the boundary in the present work (see fig. 4). Therefore, the first clusters to be formed during cooling should be very close to the boundary, and certainly inside the 7 μm etched zone. However, at some time during cooling, some clusters are formed outside this 7 μm zone and these act as sinks for diffusing complexes, preventing them from reaching the etched trough. As cooling proceeds, this blocking mechanism is enhanced, since at low temperatures, there are more clusters nucleated outside the etched region. Therefore, the proportion of complexes which could not reach the etched region is higher at low temperatures i.e. dC_B in equation 8 increases.

As discussed before, as the solute gradient is built up during cooling, there must be a tendency for the solute atoms to diffuse away from the etched region. This diffusion process is of course, more effective at high temperatures for two reasons: (i) normal temperature-dependence of a diffusion process; (ii) solute clusters are less stable at high temperatures. Therefore, the diffusion mechanism should lead to a loss of solute atoms from the etched region which decreases with decreasing temperature.

Thus, C_B is dependent on at least two mechanisms which have an opposite behaviour when temperature decreases. At high temperatures there are no stable clusters and the first mechanism is negligible while the diffusive process is dominant. Upon cooling, the blocking mechanism becomes more and more effective while the back-diffusion process loses its efficiency. This can explain why the combination of these two mechanisms is rather independent of temperature, and why the constant k in equation 4 remains constant during cooling.

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