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Diffusion in a temperature gradient – A single cycle method to determine frequency factor and activation energy of solid diffusion coefficients in alloys

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ABSTRACT

An experimental procedure for determining the temperature dependence of diffusion coefficients in a single diffusion heat treatment is introduced. Diffusion in a temperature gradient in samples with initially symmetric "roof-shaped" concentration profiles of a suitable length scale and concentration range yields asymmetric profiles that allow the determination of the frequency factor D_0 and the activation energy Q_D. The binary system Al–Cu is used as an example. The procedure is applicable to alloy systems with finite solute solubility.

1. Introduction

We introduce a new method to determine diffusivities (frequency factor D_0 and activation energy Q_D). For some alloy systems it is nowadays possible to compile D_0 and Q_D for impurity diffusion and interdiffusion from first principles [1,2], but in most cases it is indispensable to determine diffusion coefficients experimentally at different temperatures and extract D_0 and Q_D employing the Arrhenius relation. The acquired values of D_0 and Q_D are viewed as empirical approximations [3], and their accuracy strongly depends on the temperature range in which diffusion was investigated, and on the accuracy of each single measured value which is found to vary by up to one order of magnitude in different samples [4]. Reliability and accuracy of D_0 and Q_D are generally enhanced by evaluating several diffusion samples at each temperature. Thus, the experimental effort of conventional methods is high, since a considerable amount of diffusion heat treatments and sample analysis has to be carried out. Due to the high experimental effort, often less reliable data with a relatively low number of experiments are reported. Commonly, all the existing methods are analyzing concentration profiles after isothermal diffusion. Concentration measurements are carried out on sectioned slices [5–7], ground or sputtered cross sections [8,9] or along longitudinal sections [10,11]. The concentration measurement method depends on the expected concentration range. For very low concentrations, -counting of radioactive tracers or mass- and optical spectroscopic methods are used [12]. When aiming at interdiffusion coefficients, the concentrations are generally above 0.2%, and profiles can accurately be measured by Energy Dispersive X-ray Spectroscopy (EDS).

In this work we present a method that allows the determination of D_0 and Q_D in a single experimental run of annealing in a temperature gradient. Temperature and concentration gradients were utilized in an earlier work to determine ternary solid/solid phase equilibria [13]. Now this approach is extended to generate diffusion profiles with the aid of temperature and concentration gradients that contain information on the diffusivities over a chosen temperature range.

Al–Cu is the alloy system of choice to validate the new experimental approach. Cu is among the most important alloying elements in Al alloys. Thus, the temperature dependence for impurity diffusion and interdiffusion has been measured frequently and thoroughly by different isothermal methods [5–7,10,8,9,14,11,15,16]. It will be shown that the new method is capable of determining reliable parameters D_0 and Q_D for interdiffusion of Cu in fcc-Al offering distinctly reduced experimental effort.

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2. Experimental set-up and procedure

Concentration profiles in the sample are generated by repeated mushy-zone resolidification in a temperature gradient. The initial alloy Al–2 at.% Cu was melted from the pure elements Al and Cu with a purity of 99.99 at.% and cast in a rod-shaped mold with 8 mm diameter. After annealing at 540 °C for 100 h, chemical homogeneity and a coarse grained microstructure were obtained, and the rod was placed into a tube-shaped alumina crucible. The upper part of the sample was heated by a high frequency induction furnace until it completely melted, while the lower end was water cooled and remained completely solid. This technique causes complete mixing of the melt and allows precise control of the temperature gradient by adjusting water level, water temperature and heating power (Fig. 1(a)).

Between the liquid and the solid parts of the sample, there is a mushy-zone with an increasing fraction of solid towards lower temperatures. Equilibration at the solid/liquid interfaces leads to a concentration gradient according to the local solidus/liquidus concentration and mass transport of solute toward higher temperatures [18,19]. Reduction of solute content due to the mass transport out of the mushy-zone leads to its complete re-solidification during holding in the temperature gradient [18–24]. After a specific holding time that can be empirically determined or simulated [25], depending on alloy composition and temperature gradient eventually a planar solid/liquid interface develops.

The Cu concentration in the former mushy-zone decreases from lower to higher temperatures according to the corresponding local solidus concentration. As shown in Fig. 1(a), the sample exhibits the initial Cu concentration in the cold part where it remained solid, in the resolidified mushy-zone the concentrations adjust to the solidus line and form a concentration ramp [20], and at the solid/liquid interface the concentration changes from the solid to the liquid equilibrium concentration. Lowering of the sample at an adequate low velocity causes directional solidification (DS) with a planar interface. The DS step occurs in the present case under Scheil conditions i.e. complete mixing in the melt (due to forced convection by inductive heating) and negligible diffusion in the solid [17]. Thus, adjacent to the concentration ramp of the former mushy-zone, solidification proceeds with initially low solidus concentration and flat concentration gradient which is typical of Scheil type concentration profiles (Fig. 1(b)). The DS length is about 20 mm; the remaining melt is then cooled rapidly. The sample is then turned upside down and placed into the same set-up such that the part of the sample that remained solid during the previous solidification procedure is now liquid and the newly formed mushy-zone is adjacent to the concentration ramp produced in the first gradient annealing step. The highlighted part of the concentration profile in Fig. 1(b) is then mirrored by re-solidification of the second mushy-zone and subsequent directional solidification at this second position. After this procedure the sample exhibits a concentration profile with two ramps that form a roof-shaped profile and two adjacent low concentration zones (Fig. 1(c)). This sample is from here on termed "roof profile" (RP) sample.

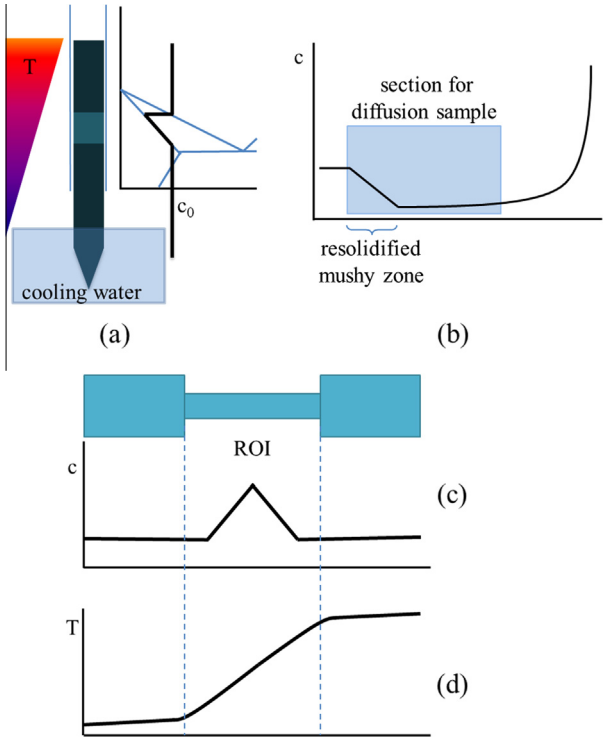

Fig. 1. Experimental set-up with concentration and temperature distribution related to the phase diagram after resolidification of the first mushy-zone (a), concentration profile after subsequent directional solidification under Scheil conditions [17](b), sample shape with roof-shaped concentration distribution after turning the sample upside down and resolidification of the second mushy-zone (c), and temperature gradient for diffusion heat treatment (d).

Additionally an Al–Cu sample with a homogeneous copper distribution of 0.7 at.% was produced by casting and annealing at 540 °C for 100 h. This sample was used as reference to access the influence of thermomigration on the Cu distribution during holding in a temperature gradient. A longitudinal section was prepared for each sample and characterized with respect to the concentration distribution by EDS. On the RP sample, hardness indentations were placed at both ends of the section with the aim of correlating positions with later measurements. The exact knowledge of the initial concentration distribution is a prerequisite for the method introduced in this work.

The samples were machined to a diameter of 3 mm in the center part. This is the region where a temperature gradient for diffusion annealing is adjusted later. The end parts of the samples remain with their original diameter of 8 mm to enhance heat transfer into the sample on one end and out of the sample on the other end (Fig. 1(c)). The longitudinal sections for EDS analysis were preserved for a second concentration measurement after the diffusion annealing. For the RP sample, the concentration profile is centered in the reduced diameter region (Fig. 1(c)). Thus, the region of interest (ROI) is situated in the sample area where a linear temperature gradient is expected (Fig. 1(d)). To check and adjust the local temperatures, three holes for thin thermocouples (0.5 mm diameter) were drilled in the samples with a distance of 6.5 mm from each other. The hole diameter of 0.6 mm and depth of 1.0 mm can be safely assumed to have negligible effect on the local temperature distribution. Type K (NiCr/Ni) thermocouples were placed in the holes. An alumina based gas tight high temperature ceramic adhesive was used to fix the thermocouples and seal the whole surface of the sample from air except the end that is cooled during annealing. On the other end of the sample, heating wire was coiled around the thin alumina layer and fixed with the alumina adhesive. For the diffusion annealing, the samples with the attached thermocouples and heating wires were transferred into an insulated box, such that only the bare end surface reached out of the insulation. The heating wire ends were connected to a controlled power supply. The temperatures measured in the ROI were displayed and recorded.

The temperatures were adjusted from 450 °C to 610 °C in the ROI, which yields a temperature gradient of 7.4 K mm^{-1}. All concentrations in the ROI were in the single phase fcc-Al field in the