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Received 22 July and accepted 28 August 1970

Letters

A Thermoelectric Method for Measuring Inhomogeneities in Metallic Solid Solutions

In the study of many metallurgical phenomena, measurements of fine scale solute variations are necessary. Generally, the more common methods of direct analysis which can be applied to very small volumes suffer from low sensitivity, particularly when the base concentration level of the solute to be analysed is small. Fine scale measurements of mechanical properties (e.g. microhardness) are not directly related only to solute concentration.

In connection with a program of non-equilibrium grain-boundary segregation studies, the use of microscopic electrical point measurements was reconsidered. There have been attempts to measure the local thermoelectric emf between a fine point and the specimen surface [1, 2], which, however, were not reproducible enough to obtain a satisfactory calibration of emf versus concentration [2]. We present here the design of a comparatively simple experiment based on the thermoelectric emf method which provided quite satisfactory results.

Similarly as in [1, 2] a modified microhardness tester (LEITZ "Durimet") was used, but in this case the thermoelectric probe was heated by means of a focused light source (fig. 1). After insulating the compound stage, the sample was mounted on a holder and both were fastened by Plasticine to the stage, and provided with the soldered output copper wire. For the heated electrode a nickel-plated martensitic sewing needle was used, whose tip was ground on a precision lathe from the original 0.04 to 0.06 mm radius down to 0.005 to 0.008 mm. Heat was supplied by focusing the light of a projection bulb with condenser (not shown) by means of a short-focus convex lens, transparent to infrared, onto a blackened copper target soldered to the needle together with an output copper wire. The sample was shielded (against heating and solder evaporation) from the light target by a thin Teflon sheet. Provided that the bulb power was stabilised and air draughts avoided, a uniform probe temperature between 250 and 350°C could be obtained. To avoid conductive heat losses to the hardness tester, the needle was mounted in a holder of machineable ceramic and the original mount for the hardness indenter was replaced by an acrylic fitting. The moving lever of the tester was equilibrated by the auxiliary loads and was loaded in the range of 1 to 10 g by means of laboratory weights.

The instrument stage was moved uniformly with the speed of about 0.1 to 1 mm/h by means of a geared timing motor and the micrometric shift of the tester (not shown). The output thermoelectric emf was recorded by the potentiometric recorder with 1 mV full scale sensitivity. This low thermoelectric emf represents the difference-signal resulting from the individual voltages of different joints in the chain and provides enough sensitivity for following slight thermoelectric emf changes caused by changing composition of the specimen in the place of the

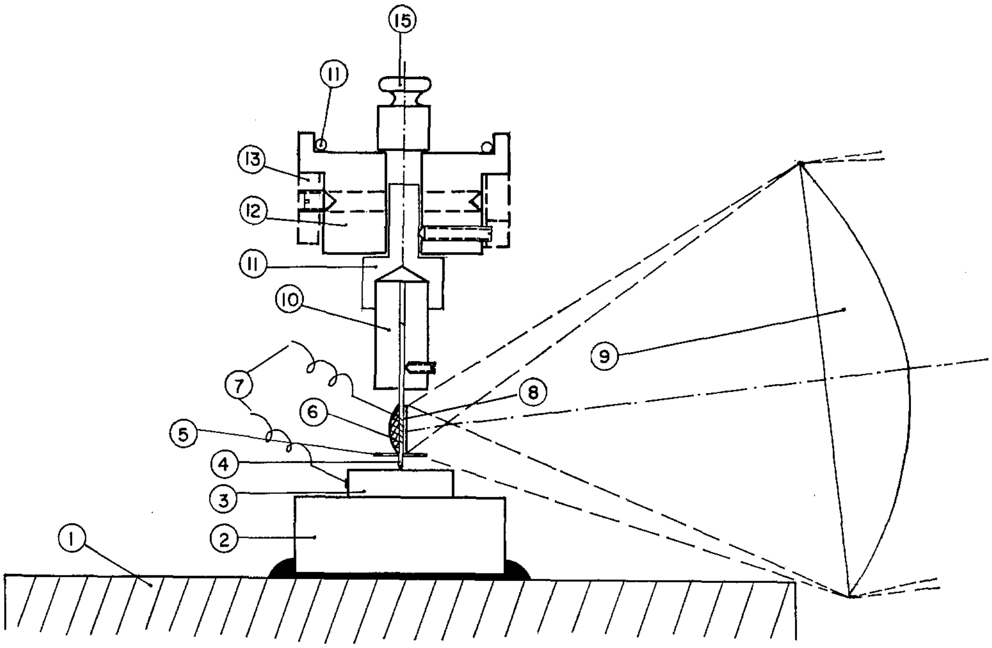

Figure 1 Schematic diagram of the measuring arrangement.
1 Microhardness tester compound stage, insulating sheet; 2 Sample holder and heat-sink; 3 Sample; 4 Measuring needle; 5 Teflon shield; 6 Soldered thermal and electric contact; 7 Thermoelectric voltage output wires; 8 Heating target; 9 Focusing lens; 10 Insulator (ceramic); 11 Fitting piece (brass); 12 Centring holder (acrylic); 13 Microhardness tester centring head; 14 Auxiliary load; 15 Loading weights.

tip contact. Absolutely clean tip and specimen surfaces are necessary for these measurements. Acetone-swabbing of these parts before each experimental run was found to be sufficient.

For the testing of the above arrangement a dilute alloy of phosphorus in copper was chosen for several reasons. First, because of strong changes of the residual resistivity and thermoelectric emf [3] with the phosphorus content in copper [4]; second, because it was expected that in this alloy non-equilibrium segregation to grain boundaries would be quite pronounced [5, 6]; finally, because to our knowledge, no diffusion data exist for phosphorus in copper.

A master alloy with 0.583 wt % phosphorus was prepared, which is below the reported solubility limit at 300°C [6] and used for the sensitivity calibration and diffusion measurements; another alloy with 0.115 wt % phosphorus was prepared for boundary segregation experiments.

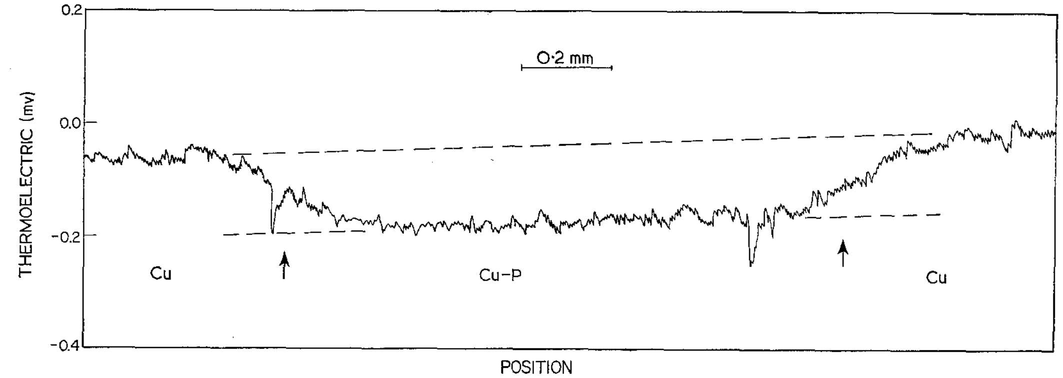

Figure 2 Thermoelectric emf course across the double diffusion couple of Cu and Cu-0.583 wt % P alloy. Position of interfaces indicated by arrows. Movement of the tip left to right, size of scratch about 11 μm.

The sensitivity and reproducibility of the method was tested on a Cu/Cu-P/Cu double diffusion couple, which after annealing at 800°C/15 h and mechanical polishing, yielded the characteristic double-semi-infinite diffusion profiles [7] shown in fig. 2. The concentration sensitivity is about 0.24 mV/wt % phosphorus, high enough for observing concentration differences of at least 0.05 wt % phosphorus. The thermoelectric emf itself was not accurately reproducible for different samples, using the same tip and heating conditions, because of different compensating contributions due to the changes of the heat transfer conditions. However, the *difference* was quite stable, slightly decreasing with the width of scratch produced by the drawn tip (in the above case 11 μm). The resulting diffusion depth $\xi = 2\sqrt{Dt}$ of about 0.18 mm then corresponds to a diffusion coefficient of $D(800°\mathrm{C}) \simeq 1.5 \times 10^{-9}$ cm^2/sec, in accordance with the reported range of values of D for other elements diffusing in copper [8].

The sensitivity of the present analytical method having been established, samples were prepared to test if this method could also be employed to detect non-equilibrium boundary segregation as discussed recently by Bercovici *et al* [9]. For this purpose, a copper-0.115 wt % phosphorus specimen was annealed 1020°C/4 h and cooled at an initial rate of approximately 15°C/sec. Near the grain boundaries a solute enrichment (fig. 3) of about 0.45 wt % phosphorus was detected (scratch size was 10 μm, about the same as in the above calibration measurement). The distribution width of about 40 μm corresponds to the region of increased microhardness which by Aust *et al* [5] was attributed to solute segregation.

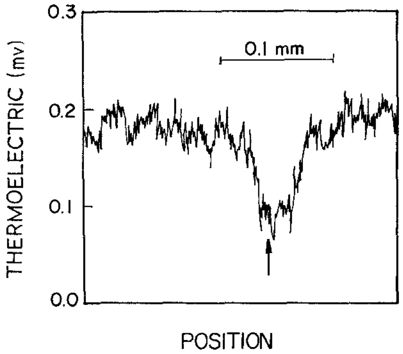

Figure 3 Thermoelectric emf course across the grain boundary in the Cu-0.115 wt % P alloy. Position of grain boundary indicated by arrow. Movement of the tip left to right, size of scratch about 10 μm.

Finally, experiments were performed to determine if the thermoelectric emf was solely a function of the alloy composition and not of the metallurgical state of the material. Measurements were performed on annealed samples which were subsequently given a heavy and localised cold deformation. Measuring over the cold-worked and annealed regions, no difference in the thermoelectric emf was detected. With the present technique it was also possible to determine solute concentration changes in non-homogenised as-cast samples of the copper-phosphorus alloys which could be attributed to segregation during solidification.

In the same arrangement the ohmic emf caused by a constant current through the tip contact could also be measured. In this case the measured emf is more sensitive to the quality of the contact and does not correspond to the local composition, but rather to its average over a small adjacent specimen volume.

The method described here enables the measurement of concentration inhomogeneities of about 10^{-2} wt %, quite comparable for instance with careful electron microprobe measurements [10]. Although the effective volume of this method (scratches of size below 5 μm can be achieved) is still larger than in the case of microprobe, the ease of the thermoelectric emf measurements is apparent. Detailed measurements of the temperature-dependence of the diffusion coefficient for phosphorus in copper as well as further experiments connected with non-equilibrium segregation phenomena at grain boundaries are in progress.

This research was supported by the National Research Council of Canada.

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Received 6 June
and accepted 1 July 1970.

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Hollow Crystals of CdSe

An open-tube technique to grow hollow prisms of CdSe is reported.

Under particular conditions, hollow crystals of II-VI compounds have been deposited from the vapour phase. Up to now it is not clear which growth mechanism is responsible for this anomalous morphology, since a broad variety of experimental conditions have been invoked.

Hollow forms of ZnS were first described [1]. Then many authors referred to the growth of hollow crystals of CdS employing open-tube techniques [2-5] as well as static techniques [6-7]. In many cases the presence of impurities seems to play an important role and hollow crystals of CdS doped with Na [2, 4], Ga or In [3], or I [5] have been successfully prepared.

Here we shall refer on the growth of hollow CdSe crystals, obtained by an open-tube technique without any added impurity.

20 g of CdSe powders (99.999% pure) purchased from E. Merck AG, were placed in the middle of a 120 cm long, 2 cm-inner diameter quartz tube and kept well packed by quartz wool. The charge is heated at 1048 ± 1°C while a very rapid flow of argon (8 to 10 l/h) is forced to pass through the charge. In a colder zone of the tube (700 to 750°C) hollow prisms, like those reported in fig. 1, are deposited in about eight hours, together with platelets and solid prisms. All the crystals are grown radially from a polycrystalline crust which coats the inner walls of the tube. The size of the hollow prisms is ranging from 8 to 12 mm in length and 0.4 to 2.5 mm in width. A spectrochemical analysis did not reveal a difference in the impurity content among the various forms of crystals.

Figure 1 Some hollow prisms (supported in wax for the photograph).

Acknowledgement

This work was supported by Gruppo Nazionale di Struttura della Materia del CNR. The author is indebted to Mr G. Zuccalli for help in preparing the crystals.

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Received 12 June
and accepted 15 July 1970

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