

Dynamic X-radiography of liquid sodium

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The dissolution process of gold and silver wires in liquid sodium was observed as an example of a system in which there is a high density difference between solvent and solute. The solidification sequence of the alloys formed by the dissolution process was also observed. Sodium is very difficult to analyse metallographically, using optical microscopy or electron beam techniques, due to the high reactivity of sodium with the water vapour present in the air. In this work, a method was evolved for observing the behaviour of liquid sodium, when used as a solvent in dissolution experiments, utilizing X-radiography. Sample cans were irradiated with a beam of X-rays and the transmitted beam fell on a fluorescent screen image intensifier. This was either viewed directly using a closed-circuit TV system or recorded using video recording equipment. In the future it is hoped to extend this work to other light-heavy metal systems such as the Al–Cu alloys.

1. Introduction

The dissolution of solids in liquid metals is a key phenomenon for the identification of a number of metallurgical processes such as the control of the as-solidified structure of the melt. For example, it has been reported [1] that non-ferrous alloys are receptive to grain refinement by like-metal inoculation, i.e. the addition of solid of Metal A to liquid of Metal B where A and B are chemically similar metals generally appearing in close proximity to one another in the periodic table, such as nickel and copper. Work carried out on dissolving a vertical wire in a liquid metal [2] indicated that one of the major factors influencing dissolution was the relative movement of the melt liquid to the inoculant. This movement is impossible to observe dynamically in most metallurgical systems and may only be inferred from results.

In an earlier experiment, where a glass rod coated with KMnO_4 was placed in a beaker of motionless water, convection was observed to have a marked effect even when the approximate density difference was probably less than 10%. (It is appreciated that KMnO_4 is not the ideal model for the solute.) The dissolving KMnO_4 produced a distinct plume of material at the bottom of the rod and there was little transport of the solute into the bulk solvent in any other region.

Thus the present dynamic radiography experiments were set up to investigate and observe any convection which may occur in metal systems during dissolution experiments where the density difference between solute and solvent is large and known accurately. They were also set up to examine the potential utilization of X-rays for observing mixtures of liquid and solid sodium and alloys.

2. Experimental procedure

There were two series of experiments undertaken.

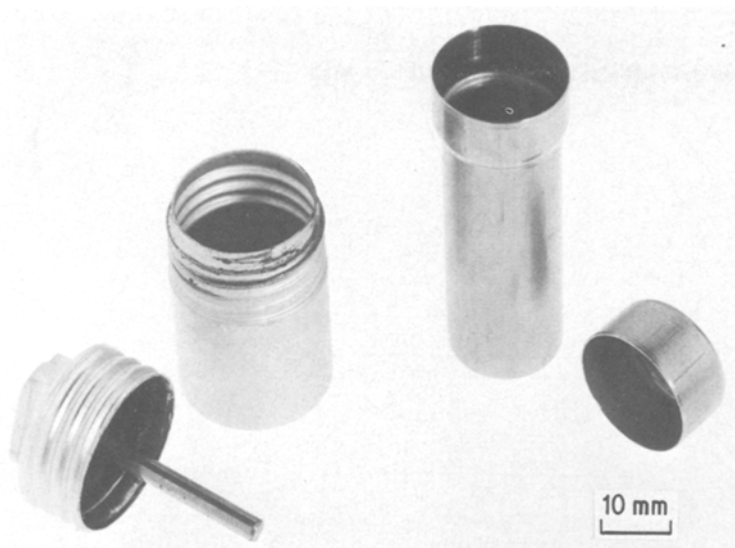
In Series 1 the dissolution couple was set up by first soldering either a gold or silver 3 mm wire to the lid of a 12 mm diameter nickel can. The can was of wall thickness 0.3 mm and 30 mm length. The lid was inserted into the can which had been filled with liquid sodium at 110°C a few seconds previously and then welded onto the can.

In Series 2 an aluminium isotope can of similar dimensions was used with the lid being screwed onto the can rather than welded. Another small difference was that the wire was pushed into a hole previously drilled into the solid part of the lid. Fig. 1 shows an aluminium and a nickel containment can.

In the experiments where the solute was silver, the containment can used was nickel.

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Figure 1 Aluminium and nickel containment cans.



Where the solute was gold, aluminium cans had to be used as the dissolution rate was so rapid that the heat input from the welding of a nickel can promoted dissolution of the gold to such an extent that the sodium became saturated with respect to gold before it could be observed using X-ray techniques.

It should be noted here that whatever the containment material the thickness of the can must be such that it does not interfere seriously with the transmission of the X-rays.

To start the run the can was placed on a pre-heated hot-plate adjacent to the X-ray source and the temperature of the can monitored by means of a chromel–alumel thermocouple placed on top of the can. The temperature of the can was raised in this manner at a rate faster than 100°C per minute. The temperature difference between the top and the bottom of the can was undetectable.

The X-ray source was then switched on so that the dissolution could be observed by fluoroscopy. The X-ray set was an XMH, Harwell custom built, (0 to 100kV, 0 to 0.5 mA) set with a focal spot of around $5\mu\text{m}$ being achieved by electrostatic and electromagnetic focussing techniques. The X-ray energy for this particular work was 80kV at 0.2mA. This beam of X-rays was directed through the sample can and the transmitted intensity collected by a Philips 150 mm fluorescing screen image intensifier and through to a Bosch video TV camera. Both series of experiments were recorded on conventional video recording equipment connected to the TV camera. There was a

magnification of $2\times$ within the image intensifier and by adjusting the geometry of the camera, can and source a total magnification of $16\times$ could be achieved. This leads to a net real resolution of 0.06mm. After a given time the power to the hot plate was switched off and the solidification sequence of the sodium–silver sodium–gold alloys could be seen. The gold solute experiments were carried out at approximately 120°C and the silver solute experiments at approximately 360°C .

3. Analysis and results

3.1. Published data

Although reliable solubility data is available for the sodium–silver and sodium–gold systems [3] as are also the equilibrium phase diagrams [4] there is no information on the rates of dissolution or the mechanism of dissolution known to the author at this time.

3.2. Series 1

In this series of experiments nickel cans were used and the solute was silver. By using fluoroscopy a reproducible plot of corrosion against time can be made, see Fig. 2. Since the rate of dissolution is related to the solute content of the solvent, it is obvious from this plot that there is a vertical concentration gradient in the sodium. This vertical concentration gradient is visible, with difficulty, on the video recordings during the dissolution stage of experiments but becomes much more easily observable in the solidification sequence. So, although no pluming of material

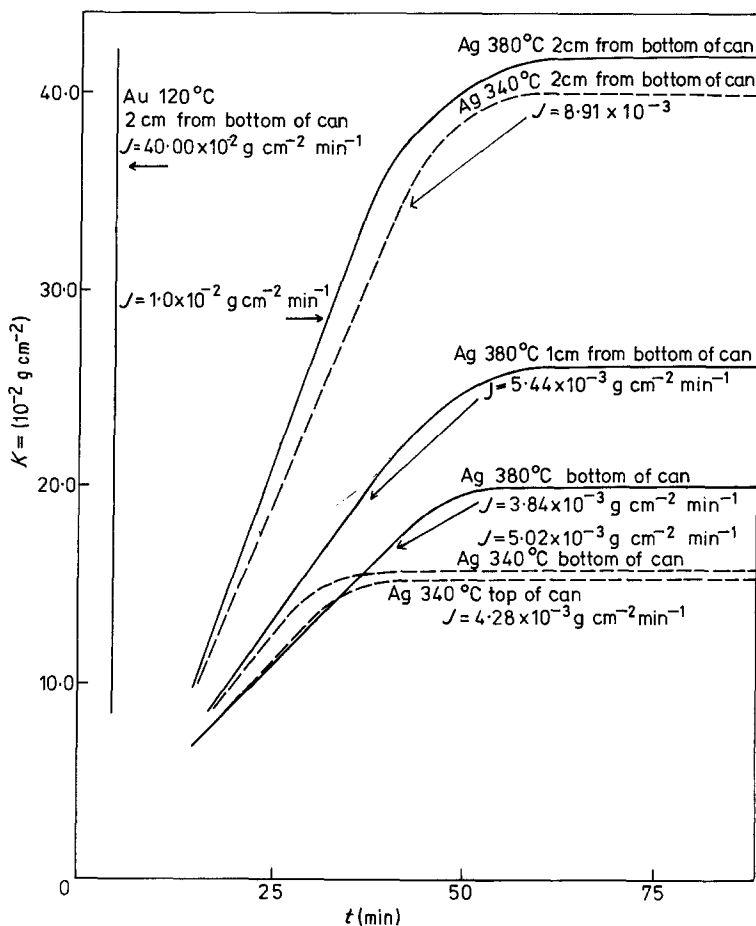


Figure 2 Graph of corrosion, K , against time, t , in liquid sodium.

was resolved (it is assumed that the equipment is sensitive enough to record if it was present), the presence of a concentration gradient could be established. By taking a stereo pair image of the solidified can, i.e. two still X-ray images of the same can in the same beam, can and photoplate position geometry but rotating the can by approximately 3° between exposures, and using a stereo pair viewer the exact position and morphology of the precipitates formed on solidification could be established. It was found that the precipitates were plate-like and were concentrated around the centre wire and the periphery of the can. They concentrated on these two areas because of (a) nucleation on the cooler can wall and (b) high solute concentration around the central wire. The exact nature of the precipitates and their position would have been very difficult to examine by any other method.

3.3. Series 2

In this series of experiments aluminium cans were used and the solute was gold. Again a reproducible

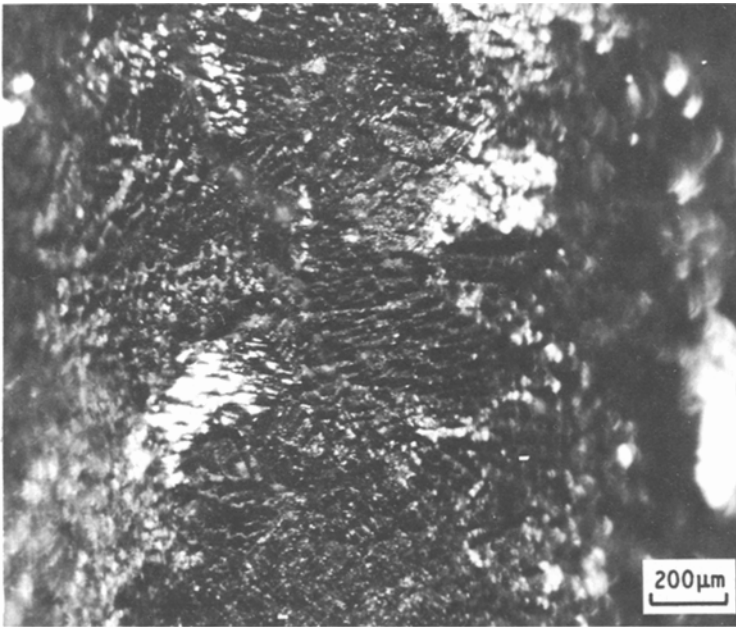
plot of corrosion against time could be made. In this system a plume of material could be observed and it is thought that the plume phenomenon is perhaps only seen where the dissolution is relatively rapid. Because of the X-ray opacity of the gold-rich solution and the vertical concentration gradient, it was not easy to measure the decrease in diameter and hence corrosion of the solid wire in the lower regions of the can.

This series of experiments did, however, mirror the KMnO_4 experiments more accurately than the former series, since the gold-rich sodium filled up the can from the bottom as more gold was dissolved. Because of the high density of the gold it became impossible to see any metallurgical structure in the molten or solidified gold sodium alloy. Thus these Series 2 experiments illustrated the drawback to fluoroscopy techniques if the ratio of the solute solvent densities is around 20:1.

3.4. Quantitative analytical techniques

One of the major problems with sodium systems is the reactivity of sodium with the water vapour

Figure 3 Reclaimed silver wire showing faceted surface.



present in the air. All experiments had to be carried out in sealed containers and therefore it is impossible with the electron beam techniques now available to observe the profiles of the solute in the sodium through these containers. For this reason the sodium cans were not quenched rapidly after any run as the profile, even if quenched-in, would be very difficult to quantify. Also as the rate of dissolution was observed *in situ* by the fluoroscopy technique the need for each run to be stopped instantaneously was eradicated. Whilst quantitative dissolution rate data could be obtained by direct measurement from the TV monitor, information on the composition of the silver-rich precipitates could only be postulated from the phase diagram. It was deduced from the corrosion curves that at the temperatures used the equilibrium concentration of solute in solvent, given by the phase diagram, was achieved after a given time. When this concentration was reached the dissolution stopped. In the silver experiments at approximately 360°C the expected silver concentration should be about 10 wt% and indeed this was the weight percentage of silver dissolved.

The reclaimed silver wires had a marked faceted appearance whereas the gold sodium interface appeared smooth at the optical level, see Fig. 3. Fig. 4 shows the plume of gold-rich sodium in the dissolution experiment.

4. Discussion and conclusion

The two systems studied show a wide range of dissolution. The rate of gold dissolution was at least an order of magnitude faster than the silver and indeed faster than that predicted by diffusion-controlled dissolution theory. The silver, however, dissolved more slowly than predicted by this theory. This would seem to indicate an interface controlling mechanism for the silver sodium system and a mass transfer controlling mechanism for the gold sodium system [2].

This fluoroscopy technique has given an insight into the process of the dissolution of solids in liquids under these particular experimental conditions and this would indicate that it is a technique worth developing for use in metallurgy.

5. Possibilities for the future

As previously stated there are drawbacks to this system such as the need for a marked density difference between, say, the solute and solvent. Another obvious problem is the need for the containment receptacle to be transparent to X-rays. Having stated these two problems, it should be possible to design cells where some of the lower melting point alloys can be observed and studied during solidification. The aluminium-copper alloys are an example of these. The Al-Cu system has also the advantage of being a well-researched model system for solidification phenom-

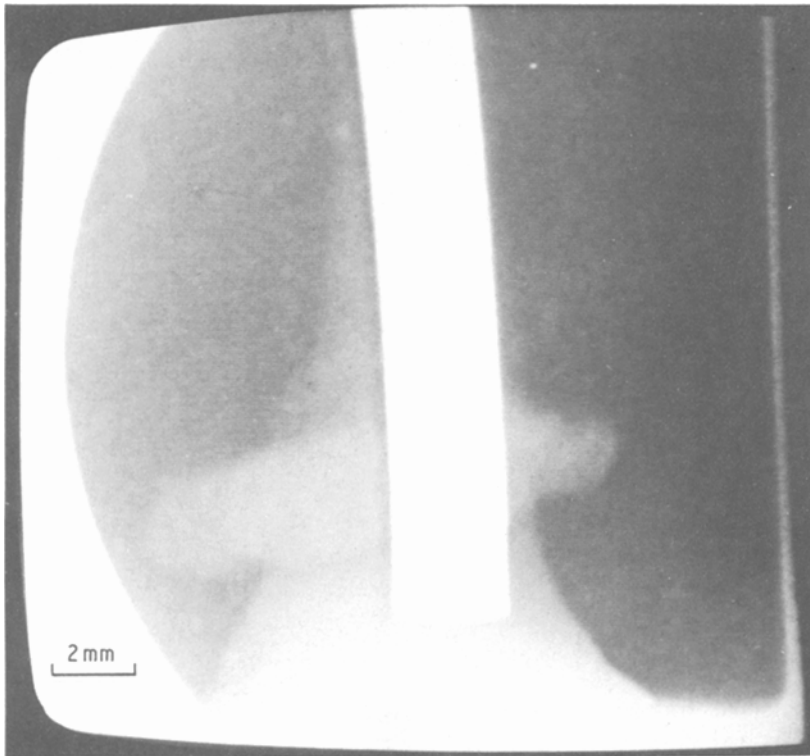


Figure 4 Plume of gold-rich sodium falling from central solute wire.

ena. For higher density liquids, e.g. iron, the cell would have to be very thin and thus far removed from reality.

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