Liquid metal penetration at grain boundaries: Characterization by synchrotron radiation micro-radiography and micro-fluorescence

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Abstract - The penetration of liquid metals into the grain boundaries (GB) of solid metals in the absence of external stress is a process which, in the case of some specific couples, can lead to severe embrittlement of the solid. We present in this paper two synchrotron radiation (SR) X-ray imaging techniques, which are well adapted for the non-destructive bulk characterization of this type of phenomena. Synchrotron radiation X-ray micro-radiography was used to characterize the liquid metal penetration kinetics in the Al/Ga system. It was shown that this modern variant of absorption radiography provides sufficient spatial and temporal resolution to observe the penetration of sub-micrometric liquid Ga films into the grain boundaries of Al bicrystals. Synchrotron radiation X-ray micro-fluorescence on the other hand is well suited for the element specific characterization of extremely dilute systems. At the expense of temporal and spatial resolution, this technique allows one to detect minute quantities of atoms, diffusing along the GB of solid metals.

Résumé - Pénétration d'un métal liquide aux joints de grains de métaux solides : étude par micro-radiographie et micro-fluorescence synchrotron. La pénétration des métaux liquides aux joints de grains de métaux solides en l'absence de contrainte extérieure peut, pour un certain nombre de couples spécifiques, conduire à la fragilisation du solide. Nous présentons dans ce papier deux techniques d’imagerie synchrotron qui sont bien adaptées pour observer ce type de phénomène. La micro-radiographie synchrotron a été utilisée pour caractériser la cinétique de pénétration pour le couple Al/Ga. Nous montrons que la version moderne de radiographie par absorption possède la résolution spatiale et temporelle adéquate pour étudier la pénétration de films sub-microniques de Ga liquide localisés aux joints de grains de bicristaux d'aluminium. La micro-fluorescence synchrotron est quant à elle bien adaptée pour la détection de traces d’éléments dans des systèmes très dilués. Au détriment de la résolution spatiale et temporelle, cette technique permet la détection de quantités infimes d’atomes diffusant aux joints de grains de métaux solides.
1. INTRODUCTION

Rapid penetration of a liquid phase along the grain boundaries (GB) of a polycrystalline solid can be observed in a number of metallic systems like AlGa [1], Ni/Bi [2], CuBi [3]. This phenomenon occurs in the absence of any external stress and results in the formation of up to micrometer thick wetting layers at the grain boundaries. It is very likely that grain boundary penetration is also involved in the process of Liquid Metal Embrittlement (LME) [4-6], which corresponds to the accelerated growth of sub-critical cracks in stressed specimens in a liquid metal environment.

In spite of numerous investigations the key mechanisms, which are at the origin of the rapid penetration, are not clearly identified and still controversially discussed [7-9]. So far, none of the proposed models seems to correctly account for the experimental observations. This stems also from the fact that direct observation of the penetration process is very difficult since the phenomenon takes place in the bulk of the sample.

From this point of view, synchrotron radiation micro-imaging has proven to be a rather adequate tool: X-rays penetrate deeply into the material and allow one to perform in-situ observations in the bulk of millimetre sized samples [10].

After a brief presentation of the experimental techniques used in this paper (micro-radiography and X-ray micro-fluorescence), we present the results obtained during our in-situ micro-radiographic observations of the penetration of liquid Ga in Al bicrystals (§3). We then show the complementarities between micro-radiography and micro-fluorescence imaging for the study of sub-micrometric GB wetting (GBW) layers in the Al/Sn system (§4) and in the Ni/Bi system (§5).

2 EXPERIMENTAL TECHNIQUES

2.1. X-ray micro-radiography

The in-situ imaging experiments were carried out at beamline ID19 [11] of the European Synchrotron Radiation Facility (ESRF). ID19 is devoted to high resolution imaging and features an energy tunable (7-100 keV) X-ray beam of low divergence (~ 1 μrad). The incoming 'white' synchrotron radiation was monochromatized to 15 keV using a Rb-B4C multilayer with large energy bandwidth (Δλ/λ=10⁻²). The X-ray image is converted into visible light by means of a fluorescent screen (25 μm thick LAG: Eu crystal) which provides a spatial resolution in the order of 1-2 μm. Conventional microscope optics are used to project the image on the cooled 1024² CCD camera, with a dynamic range of 13 bits, fast readout (0.06 s/frame) and low dark current (3 e⁻/s) [12]. In this configuration a maximum frame rate of 10 images per second can be achieved while maintaining a good signal to noise ratio in the recorded images.

2.2. X-ray Micro-fluorescence Imaging

The X-ray fluorescence experiments [13] were carried out at beamline ID22 [14] which is equipped with different types of focussing X-ray optics in order to produce highly intense and micrometer sized X-ray spots (between 1 and 50 μm, depending on the X-ray energy and the type of optics used). By scanning the sample point by point through the beam and recording at each position the emitted X-ray fluorescence spectrum, one can map out the two-dimensional elemental distribution. Figure 2 shows a scheme of the experimental setup for this kind of experiments. The incoming polychromatic synchrotron radiation is monochromatized by means of a double crystal
monochromator and a flat mirror (to cut off higher harmonic energies). With the help of compound refractive lenses (CRL) a demagnified image of the X-ray source is produced. The sample is mounted on a motorized translation stage such that it can be positioned and scanned through the X-ray focus. By translating the CRL out of the incident beam, a conventional absorption radiograph can be recorded on the high resolution detector system (CCD based, similar to the one described in the previous section) positioned downstream of the sample.

**Figure 1.** Experimental setup used for in-situ radiography imaging experiments at beamline ID19 of the ESRF. The transmitted beam is recorded on a CCD-based high resolution detector system providing up to one μm spatial resolution over a field of view of 1 mm².

**Figure 2.** Typical experimental setup for X-ray micro-fluorescence imaging: the monochromatic beam is focalised by means of appropriate X-ray optics on the sample. An energy dispersive detector is used to record the X-ray fluorescence spectrum emitted from the sample. By scanning the sample across the beam, one can determine the elemental distribution with very high sensitivity (ppm level).
3. Ga PENETRATION OF AN Al BICRYSTAL USING MICRO-RADIOGRAPHY

The penetration kinetics of liquid Ga in 99.996% Al bicrystal boundaries was investigated using synchrotron radiation micro-radiography [15]. Two 600 µm thick slices were spark-cut from Al bicrystals ingots (Ecole des Mines, Saint-Etienne, France) with two different misorientations: a general boundary (150° symmetrical tilt around <110>) and a {113} twin boundary (129°30' symmetrical tilt around <110>). To ensure the contact between Ga and the Al bicrystal, the later was dipped in a 10% KOH (ethanol) solution at 40°C to remove the oxide layer. While the sample was still in the solution, the contact (and then wetting) with a small droplet of liquid Ga (saturated with Al) was initiated. In order to freeze the penetration process at this early stage, the sample was quenched in liquid nitrogen and subsequently kept below room temperature during its mounting on the micro-radiographic set-up. The GB was set almost parallel to the X-ray beam in order to optimise the detection limit for thin penetration layers. The in-situ imaging experiments were carried out shortly afterwards, by slowly heating the sample to 30°C to remelt the Ga droplet.

An optimized acquisition mode allows to monitor the Ga penetration with a frame rate of 6.3 images per second. Figure 3 exhibits three (out of a series of about 300) X-ray micro-radiographs showing different stages of the penetration process along the general grain boundary. The initial image of the sample without Ga was subtracted logarithmically from these images. Consequently, the image contrast is directly proportional to the Ga thickness crossed by the X-ray path.

![Figure 3](image)

**Figure 3.** In-situ observation of GBW in Al bicrystal (150° symmetrical tilt around <110>). The images show the propagation and thickening of the liquid film. The boundary is almost parallel to the beam direction: the different widths at positions (1) and (2) result from a slight curvature of the boundary plane and are not connected to the thickness of the Ga layer itself.
It is worth noting that the apparent difference of the thickness of the Ga layer (e.g. positions (1) and (2) in Figure 3) is not caused by a difference of the layer thickness itself, but mainly due to a change in the local inclination $\varphi$ between the GB plane and the incoming X-ray beam. For instance the angle $\varphi$ is more important on the left-side of Figure 3 when compared to the right-side. The real Ga layer thickness corresponds to the apparent Ga layer thickness times $\sin(\varphi)$. The leading edge of the penetration front is not clearly distinguishable by eye. However, the analysis of the absorption signal, averaged over small stripes like the ones depicted in Figure 3d, allows to deduce both the penetration rate along the grain boundary and the thickening rate of the Ga film. Figure 4a shows the evolution of the Ga layer thickness versus time for three different positions (A, B and C) along the GB. Depending on the position, one can distinguish different time offsets $t$, before the arrival of the penetration front. Figure 4b exhibits the time of passage of the penetration front versus the distance from the external Ga reservoir. While the first 200 microns nearest to the Ga droplet appear to be wetted in a very short time, an almost linear dependence between distance and time is observed afterwards. One then can deduce a mean penetration speed of about 25 $\mu$m/s. The thickening rate depends on the position along the boundary and varies between 0.8 and 1.4 $\mu$m/s. The wetting layer was observed to grow up to a thickness of about 300 nm which was reached after 240 s. It is interesting to note that the product of this time with the observed penetration rate compares well with the actual length of the bicrystal (6 mm versus 4.5 mm).

![Figure 4](image)

**Figure 4.** (a) Temporal evolution of the Ga layer thickness in regions A, B and C (see Fig. 3), (b) time of passage of the penetration front as function of the distance from the external Ga reservoir.

No wetting layer could be detected for the $\{113\}$ twin boundary, even when the temperature was increased up to 200 °C. Since such $\{113\}$ twin boundary has a low GB energy, compared to a general GB, the absence of wetting should correspond to a negative wetting driving force (i.e. $E_{\text{GB}} - 2\gamma_{SL} < 0$).

The presented results clearly show the possibilities of synchrotron micro-radiography for in-situ observation of sub-micrometric Ga wetting layers. However it has to be clearly stated that the very first steps of the wetting process, involving only a few monolayers of Ga, cannot be observed with this technique. Under the current experimental conditions, a minimum layer
thickness of about 20 nm is required in order to give rise to one per cent image contrast. As briefly discussed later, TEM is certainly more adapted to observe the very first steps of the penetration process [1], even if it is restricted only to very thin foils.

To overcome the spatial resolution limitation of micro-radiography, especially to detect very thin liquid metal films, one can use synchrotron radiation X-ray micro-fluorescence [13]. The two following parts of this paper show first experiments of the combined use of synchrotron micro-radiography and micro-fluorescence to investigate liquid metal penetration.

4. GROOVING OF AN ALUMINIUM BICRYSTAL IN THE PRESENCE OF TIN: A MICRO-RADIOGRAPHY AND MICRO-FLUORESCENCE STUDY

It has been shown that the system Al/Sn displays a first order grain boundary wetting transition at about 600° C (depending on the GB energy) [16]. The mentioned results have been obtained ex-situ on a series of bicrystals cut from the same ingot. In order to evaluate the possibility of a possible in-situ observation of this wetting transition by X-ray imaging techniques, a first (ex-situ) test experiment was performed at beamline ID22, combining X-ray micro-imaging and micro-fluorescence. For this a 2.1 mm thick slice was cut from an Al bicrystal (general, symmetrical tilt grain boundary, provided by B. Straumal, Chernogolovka) which had been covered on one side with a 100 μm thick layer of tin (saturated with Al). The sample has been annealed in air at 620 C for about one hour and then cooled down slowly to room temperature. In order to remove the Sn, which covers after the annealing also the lateral sample surfaces, the bicrystal was carefully polished.

*Figure 5* shows an X-ray microradiograph (E=30 keV) showing the contact area between the Al bicrystal and the Sn layer on top of the crystal. One observes a typical thermal groove with a finite contact angle θ of about 22 degrees. Due to large difference in the X-ray attenuation coefficient, excellent contrast is obtained between Al and Sn. However, the sensitivity of micro-radiography is not sufficient to detect the small quantities of Sn, which have diffused along the GB ahead of the macroscopic groove.

In order to reveal the presence of Sn diffusion ahead of the groove tip, we switched to micro-fluorescence detection mode. For this, the incoming monochromatic X-ray beam was focussed on the sample surface by means of a set of 100 Al lenses, positioned 1.5 m upstream in the beam. The focal spot at 30 keV has an ellipsoid shape with a typical size at this energy of 50 x 10 microns. Just by translating the lenses in or out from the X-ray path, it is possible to work either in the micro-radiographic or micro-fluorescence mode without moving the sample. *Figure 5* exhibits a series of line profiles showing the number of detected Sn fluorescence counts (Sn Kα1=25.3 keV) as a function of the sample position. The measured intensity is directly proportional to the amount of tin present in the sample volume probed by the X-ray beam. It turns out that one can detect the presence of Sn up to 300 μm ahead of the groove tip. The concentration profiles across the boundary reveal also the occurrence of Sn diffusion from the GB into the adjacent grains.
5. DETECTION OF NANOMETRIC Bi WETTING LAYERS IN Ni BICRYSTALS

When liquid Bi is brought in direct contact with polycrystalline Ni, two apparently different wetting phenomena are known to take place at the Ni grain boundaries: i) slow growth of macroscopic, liquid filled GB grooves and ii) rapid penetration of a nanometric film well ahead of the macroscopic groove. The detection of the macroscopic wetting layer is straightforward and can be achieved by means of scanning electron microscopy or X-ray microradiography (see figures 6a and b). The presence of the nanometric film on the other hand could so far only be detected by means of Auger electron spectroscopy (AES) [2], which implies breaking of the grain boundary under high vacuum (ex-situ technique). The high penetration power of X-rays is a possible way to overcome this limitation: the highly energetic K shell fluorescence emission of Bi atoms (Bi K\(_{\alpha2}\): 77 keV) can go through several millimetres of Ni and the presence of nanometric penetration layers might therefore be detected in the bulk of the samples during m-situ experiments.

A first series of test experiments was performed at lower X-ray energies close to the Bi L\(_3\) absorption edge (13.4 keV) With an escape depth of the characteristic Bi L emission lines of the order of 10 µm, one can, in this case, probe the region close to the GB surface intersection. For these experiments a 100 µm thin blade was spark cut from an Ni bicrystal and it was put in direct contact with (saturated) liquid Bi during 16 h at 700°C. The sample was then embedded in epoxy and carefully polished.
Figures 6c and d show two line scans taken in the micrometric and nanometric part of the Bi penetration layer, respectively. The corresponding positions are indicated by the arrows in Figure 6a. The nanometric penetration layer can neither be detected in radiography nor in scanning electron microscopy: in both cases the macroscopic part of the GB groove seems to end abruptly. However, the X-ray fluorescence profile still reveals a weak signal, indicating the presence of a thin Bi film. Given the width of the microscopic part of the Bi wetting layer (of the order of 5 μm) and the ratio of the peak intensity values of the Bi fluorescence signal in the micrometric and nanometric part (I_{micro} / I_{nano} ~1000), one can estimate the thickness of the nanometric wetting layer to be about 5 nm. This value compares well with the thickness determined by AES, reported by Marie et al. [2].

Figure 6. (a) X-ray microradiograph of an Ni bicrystal after 16 h direct contact with liquid Bi. (b) SEM image of the end of the macroscopic Bi penetration layer. (c) Fluorescence signal (Bi - Lα) when scanning the crystal across the macroscopic penetration layer (left arrow in a). (d) Bi Fluorescence signal in the centre of the region with of the nanometric penetration layer (right arrow in a).

6. DISCUSSION AND CONCLUSIONS

The presented results clearly show the potential of modern synchrotron radiation microimaging techniques to analyse dynamic phenomena in the bulk of metallic samples.
Concerning the spatial and temporal resolution, X-ray micro-radiography is well adapted to observe the penetration of sub-micrometric liquid metal layers in GB, as shown for the Al/Ga couple near room temperature. For this system, both the kinetics of the Ga penetration along the GB and the thickening rate of the GB wetting layer were analysed: one obtains \( v = 25 \, \mu m \, s^{-1} \) and \( \frac{de}{dt} = 1 \, nm \, s^{-1} \) respectively. These values are similar to those reported by Hugo and Hoagland using in-situ transmission electron microscopy [1]. They observed, at room temperature, linear penetration kinetics \((0.1-10 \, \mu m \, s^{-1})\) and a linear thickening rate \( \frac{de}{dt} = 0.1 \, nm \, s^{-1} \) of the Ga layer.

These values are somewhat lower than those reported in the present paper, but have about the same order of magnitude (note that the penetration rate is expected to be strongly dependent upon the nature of the studied GB). It is also interesting to note that the ratio between penetration kinetics and thickening is nearly identical.

Concerning X-ray microfluorescence we presented first results illustrating the tremendous gain in sensitivity for the detection of minute quantities of diffusing and/or penetrating atoms. Comparing the interest of the two techniques, one might state that micro-radiography provides high spatial and temporal resolution over a large field of view but it does not allow observing the very first steps of the penetration process since it is only sensitive to layers thicker than about 20 nm. X-ray micro-fluorescence on the other hand allows to measure diffusion profiles and to detect the presence of nanometric penetration layers but provides only poor temporal resolution, as the information is acquired point by point by scanning the sample across the beam.

The determination of the penetration kinetics of nanometric films by means of in-situ X-ray fluorescence measurements would be very interesting for a better understanding of the involved processes. However, such measurements will be very tricky as they require special sample environments and more sophisticated sample geometries in order to minimize artefacts arising from surface wetting, evaporation, etc...

Finally it is worth noting that micro-radiography can be easily extended to its three dimensional counterpart, called X-ray micro-tomography. Micro-tomography has performed huge progresses in the recent years [10] and was recently applied to characterize Ga wetting layers in the bulk of polycrystalline Al alloys [17]. Moreover, first attempts have been undertaken to extend 2D fluorescence imaging to fluorescence tomography, a technique providing 3D information about the elemental distribution in the bulk of opaque samples. The mentioned techniques open new ways for non-destructive characterization of dynamic bulk phenomena and will allow addressing a number of problems, which could not be studied by conventional techniques.

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