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Kinetic, volumetric and structural effects induced by liquid Ga penetration into ultrafine grained Al

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ABSTRACT

Kinetic, volumetric and structural effects induced by penetration of liquid Ga in ultrafine grained (UFG) Al produced by severe plastic deformation using high-pressure torsion were studied by isothermal dilatometric measurements, electron microscopy, atomic force microscopy and X-ray diffraction. Severe plastic deformation changed the distribution of impurities and their segregation was revealed by transmission electron microscopy. Two-stage length changes of UFG Al were observed which are explained by counteracting effects of expansion due to grain boundary segregation of Ga and contraction due to precipitation and recrystallization. After applying Ga, the kinetics of the liquid Ga penetration in UFG Al is studied in-situ in the electron microscope by the "first appearance" method and the time scales are in agreement with those inducing the volumetric changes.

1. Introduction

Fast liquid penetration into the grain boundary (GB) network of a polycrystalline solid is observed for different metallic or ceramic pairs of materials [1–3]. Yet, a detailed mechanism as well as morphological features or the kinetics of the penetration process are not fully understood.

One of the most spectacular examples of liquid metal embrittlement (LME) is the catastrophic penetration of liquid gallium along aluminum grain boundaries [4] which has been termed "gallium poisoning". The Al–Ga system reveals a low mutual solubility [5], absence of intermetallic compounds and an embrittlement phenomenon due to the formation of a liquid film along GBs [6]. Formation of long narrow channels of liquid Ga with thicknesses ranging from nanometers up to several micrometers has been reported [7,8].

The kinetics of the penetration of liquid Ga along Al GBs has been studied, e.g., by Hugo and Hoaglund [8,9] and by Ludwig et al. [6,10] by means of transmission electron microscopy and synchrotron radiation microtomography, respectively. According to Hugo and Hoaglund, Ga penetrates into Al GBs in two stages: first by GB wetting and then via GB diffusion [11]. Further insights into the atomic-scale mechanism of liquid metal embrittlement were provided by Sigle et al. [12]. The cohesion loss of GBs induced by liquid Ga was studied by Stumpf and Feibelman [13] and Thomson et al. [14] by using ab initio calculations. They found that the bonding between Ga atoms is weaker than that of Al–Ga atoms leading to perfect wetting of GBs. Still, many important issues of the LME phenomenon and the particular mechanism of liquid Ga penetration along GBs of Al remain highly disputed and obscure.

GB *tracer* diffusion of Ga in Al and Al–Ga alloys (with a total Ga content up to 1 at.%) was comprehensively investigated using the ^{71}Ge and ^{72}Ga radioisotopes and the GB diffusion rates were measured to be too low to be consistent with the observed rapid penetration of Ga from a *liquid* source [15]. This fact substantiates the importance of normal stresses probably developing due to wetting of a GB by the contacting liquid layer and facilitating diffusion ahead of the crack tip [16] that evolves along the GB. The appearance of normal stresses was e.g., described by Klinger and Rabkin [17] as a Kirkendall effect due to the inequality of the GB diffusion coefficients of the matrix and solute atoms. A dramatic influence of the surface conditions on the kinetics of GB atomic transport and developed stresses was recently demonstrated [18].

Severe plastic deformation (SPD) is a well-established method to achieve grain refinement [19] and applying SPD processing to Al yields an ultra-fine grained (UFG) structure. SPD induces a large number density of lattice defects, modifying simultaneously not

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only the microstucture, but the kinetics and structural properties of GBs, too [20–22]. GB diffusion could be enhanced in the resulting UFG material by orders of magnitude [23,24], which was attributed to the free volume accumulation at the GBs [25]. The free volume recovery in ECAP-processed metals was studied recently [26,27] and the deformation-induced GB expansion was quantified as well [28]. These features, as well as residual strain at the GBs [20,21], may strongly influence the LME effect, providing further insights into this intriguing phenomenon, especially since the effect of SPD treatment on LME was not studied yet.

The present paper is devoted to an experimental investigation of volumetric, kinetic and structural effects induced by application of liquid Ga to SPD-processed UFG Al. The changes are followed by microstructure examination, texture and dilatometric measurements.

2. Experimental details

A technical pure Al 1050 alloy (see Table 1 for the chemical composition) was used. Within the text, we refer to this alloy in short hand notation as "Al". The alloy was chosen to achieve an UFG microstructure (with the grain size about one micrometer) after SPD, see below, since it is almost impossible to refine pure Al to sub-micrometer grain size at room temperature.

Discs of a diameter of 10 mm and an initial thickness of 1 mm were cut and severely deformed by high pressure torsion (HPT) applying a pressure of 4 GPa and performing 5 revolutions at the rate of 0.5 rpm.

Bars of a rectangular shape and dimensions of $8 \times 5 \times 0.84$ mm^3 were cut from UFG Al as it is sketched in Fig. 1, left. Similar samples were also cut from the coarse grained (CG) Al and were used as a reference.

A Linseis (L70/2171) dilatometer, which allows determination of the length changes with an absolute accuracy of about 100 nm was employed to measure the length variation of the deformed sample with and without application of liquid Ga under isothermal conditions. Specimens were mounted on the sample holder to prevent any additional tilting or displacement. The measurements were carried out with the long sample axis oriented along the direction of the dilatometric measurement, perpendicular to the surface where the Ga was applied (see Fig. 1, right). Before Ga application, the stability of the signal was checked for the mounted sample for 20,000 s under isothermal conditions. Then, in order to establish a direct contact between the Al sample and the liquid Ga source, the Al oxide layer was broken by mechanical scratching and a droplet of Ga (heated to about 30 °C) was applied onto this area.

The microstructure was characterized with an FEI Nova NanoSEM 230 scanning electron microscope (SEM) equipped with an electron back scatter diffraction (EBSD) detector. The sample surface was prepared by mechanical polishing using a Tegramin polishing machine and applying 0.5 μm diamond paste in the final step and subsequent electropolishing (70% perchloric acid in ethanol at 30V and 5 °C) for a short time.

The kinetics of Ga penetration in coarse-grained and UFG Al samples was examined using a "first appearance" method. Thus, both sides of the Al sample of the given thickness were polished and a drop of liquid Ga was applied on one surface (similar to its application for the dilatometric measurements). The sample was transferred into the SEM chamber and the opposite surface was monitored with respect to its structural and chemical modifications.

Table 1
Nominal chemical composition of Al 1050.

Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
(wt.%)	0.08	0.20	0.016	0.043	0.031	0.001	0.014	99.63

A Zeiss Libra 200 FE field-emission transmission electron microscope (TEM) equipped with an in-column Omega energy filter was employed. TEM samples of 3 mm in diameter were cut from the HPT-processed discs at a half radius distance from its center. The samples were thinned to 60–90 μm thickness by mechanical grinding and were finally ion milled using a precision ion polishing system Gatan (PIPS 691).

The so-called Automated Crystal Orientation Mapping (ACOM) technique that measures the grain orientations and crystallographic phases in a transmission electron microscope (TEM) was used [29]. For ACOM, a large number of nanobeam-diffraction patterns (NBDP) are required in a scanned sample area. Subsequently, every acquired NBDP is compared to a set of pre-calculated diffraction patterns for a given structure. The best match of the patterns indicates the orientation of the crystal and the relation of the pixel sum of the best image correlation to the pixel sum of the second best image correlation gives the reliability index. For the analysis, 3 sets of Al pre-calculated diffraction patterns with 100, 200 and 300 diffraction patterns were used for the correlation to test for the numerical stability of the results. ACOM data were recorded by an FEI Technai F20, 200 kV field-emission TEM equipped with the ASTAR™ software. Finally, an orientation map of 450×450 pixel^2 obtained with a spot size of 1.4 nm and an orientation resolution (~2°, depending on the actual orientation) was acquired with a 5 nm step size.

In order to investigate the surface evolution induced by the Ga application, an Atomic Force Microscope System XE-100 (PARK) with separate X–Y and Z scanners was employed. The sample was prepared following the same procedure as that for preparation of samples for SEM analysis.

Texture measurements were performed with a Bruker-AXS D8-Discover with GADDS using Cu K_α radiation (wavelength 1.54056 Å). The orientation distribution functions (ODF) and complete pole-figures were evaluated using the LABOTEX software suite.

3. Results

3.1. Dilatometric measurements

The stability of the experimental set-up as a function of time is quantified by following the length changes of a reference Al sample at room temperature over a long period of time (the black dashed line in Fig. 2). The signal, i.e., the relative length change $\Delta L/L$, is quite stable with a maximum relative deviation from the zero level of about 10^{-5}.

The volumetric changes induced by the Ga application in coarse-grained (CG) Al are measurable at room temperature (293 K), but remained comparably moderate as shown in Fig. 2a. The maximum relative changes did not exceed 10^{-4}.

This is not the case if liquid Ga is applied to UFG Al that was previously deformed by HPT. The experimental curves recorded after application of two different amounts of Ga are shown in Fig. 2a. The concentration of Ga was determined by subsequent EDX analysis in the SEM and represents a sample-averaged value. In the two cases, about 0.3 and 5 wt.% Ga were introduced, as indicated by the EDX analysis after the dilatometric measurements. Obviously, there are two major stages in the time evolution of the dilatometric curve measured for UFG Al after Ga application, which exceed by an order of magnitude the signal measured for cg-Al. The first stage indicates a sample expansion, $\Delta L/L > 0$, during the early stage of liquid metal penetration. The expansion amounts to about 10 μm