



Full length article

# Melting and solidification of lead nanoparticles embedded in Aluminium-Gallium matrices

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## ABSTRACT

Analyzing the impact of the host matrix on the melting/solidification of embedded Pb nanoparticles, various Ga concentrations (0, 1, 3 and 6 at.%) were added to the Al matrix within the solid solution regime to modify the mismatch between matrix and nanoparticles by expanding the host lattice. Using transmission electron microscopy and differential scanning calorimetry, a strong impact of an atomically flat Ga-enriched wetting layer around the Pb nanoparticles on the melting/solidification was observed. The Ga-enrichment was found to be about ~3% above the matrix level, independent of the Ga concentration in the matrix. It is concluded that upon solidification vacancies arising from the 3.3% volume shrinkage of liquid Pb are filled by the fast diffusing Ga. The Ga-enriched layer chemically and mechanically decouples the matrix from the nanoparticles leading to a more freestanding particle behavior showing strong undercooling upon solidification and reduced or no superheating upon melting.

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## 1. Introduction

Nanoparticles embedded in a matrix with mutually immiscible constituents offer ideal conditions for studying the impact of hetero-interfaces on reversible phase transitions. Al-Pb composites consisting of nanometer-sized Pb inclusions embedded in a polycrystalline Al matrix are a model system for size-dependent melting studies [1–6]. A local minimum free-energy configuration is obtained when the nanoparticles with cube-octahedral shape adopt a cube-on-cube orientation relationship with the matrix, having larger {111}- and smaller {100}-facets [1–3,7–13]. The metal/metal interfaces were found to maintain a strict cube-on-cube orientation relationship although exhibiting a large lattice mismatch of 22% [1–3,7–9]. To explain the relationship between morphology and strain, an elastic accommodation of the lattice mismatch via vacancies was claimed [8,9]. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) in-situ heating experiments have shown that the Pb melting temperature  $T_m$  of such particles can be increased by more than 60 K with respect to the bulk melting point of Pb [1–3,8,11,14,15]. The observation of an elevated melting point of nanoparticles was

correlated with faceted particle shapes, semi-coherent interfaces and pressure, whereas melting point depressions were attributed to non-faceted particle shapes [2,3,7,16,17]. It has been shown that the melting point of non-faceted Pb inclusions embedded in Al can be manipulated by an appropriate heat treatment changing the particle morphology from non-faceted to faceted shapes which then increases the melting point from below to above the bulk melting of Pb [7,18]. Such melting behavior motivates an interest in the relation between strains and interfacial morphology. The elastic strain caused by melting and solidification of small Pb inclusions in Al has been monitored by in-situ TEM [19]. When the nanoparticle is liquid, the surrounding Al matrix is free of strain. However, as the inclusion solidifies it contracts causing elastic distortions in the Al matrix, which are thought to be relieved by lattice vacancies [19]. Evidence of localized misfit via geometrically necessary dislocations has also been found [7,20,21], and the nanoparticles show reduced melting enthalpy [22]. Moreover, liquid Pb inclusions showing Brownian motion in three dimensions have been observed [23,24]. It has been shown that the motion of the Pb inclusions is controlled by volume vacancy diffusion [24].

The goal of this study is to investigate the impact of the host matrix on the melting and solidification behavior of the Pb nanoparticles. For this purpose, Ga was added to the matrix within the solid solution regime. Alloying of Ga expands the lattice of the Al

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matrix and thus reduces the mismatch between matrix and Pb particle. Moreover, Ga is immiscible with Pb [25] and thus the melting and solidification of the Pb nanoparticles was expected to be affected by the Ga addition without involving changes in the composition of the Pb nanoparticles. If the hypothesis of strain relief via accumulated lattice vacancies upon solidification holds, and the accumulated lattice vacancies required for the observed Brownian motion of the liquid Pb nanoparticles are still present, then the Ga addition is expected to show a segregation effect around the Pb nanoparticle interfaces. The present study demonstrates this. The solidification was drastically influenced by the Ga addition leading to an undercooling of more than 100 K for  $\text{Al}_{93}\text{Ga}_6\text{Pb}_1$ . Moreover, Ga segregation was found around the Pb nanoparticles, which has been shown to be independent of the nominal Ga (1–6 at.%) addition and amounts to about 3 at.% above the matrix level, thus accommodating the volume jump of 3.3% of Pb during solidification.

## 2. Experimental

Samples of  $\text{Al}_{99-x}\text{Ga}_x\text{Pb}_1$  composites (with  $x = 0, 1, 3$  and  $6$ ; all in at.%) within the solid solution regime were produced by melt spinning. Initially, ingots of approximately 3 g were prepared by arc melting under protective Ar gas atmosphere using high-purity Al (5N), Ga (5N) and Pb (5N). The ingots were then melted in a quartz glass crucible by induction melting under a low pressure Ar atmosphere. The ejection of the melt onto a rotating copper wheel (wheel-surface velocity of 31 m/s) resulted in crystalline ribbons with thicknesses of 50–60  $\mu\text{m}$ . As-cast samples were analysed by TEM and EDX directly after processing, without any heating where the nanoparticles get molten and re-solidified. The chemical composition after rapid solidification was verified by energy dispersive X-ray (EDX) analysis in a scanning electron microscope (FEI Nova Nano SEM 230) and corresponds to the nominal composition (see Table 1). For all EDX measurements the ZAF method was applied, without using standards. Calorimetric measurements using a power-compensated differential scanning calorimeter (Diamond DSC, Perkin Elmer) under constant Ar flow were performed using a constant heating and cooling rate of 20 K/min. Sample masses were typically around 30 mg. According to Vegard's Law the lattice constant of Al(Ga) can be given for pure Al, the Al-1at.%Ga, Al-3at.%Ga, Al-6at.%Ga to be 4.0496 Å, 4.0543 Å, 4.0638 Å and 4.0780 Å, respectively. Consequently the mismatch of Al(Ga) to Pb can be given for pure Al, the Al-1at.%Ga, Al-3at.%Ga, Al-6at.%Ga to be 22.2%, 22.1%, 21.9% and 21.5%, respectively.

TEM specimens for analytical STEM were initially mechanically polished with 5  $\mu\text{m}$  SiC and subsequently ion-milled at liquid nitrogen temperatures using the PIPS II (Gatan PIPS 695) with acceleration voltages from 3.0 to 0.5 kV and incident beam angles of 4° for top and bottom. STEM imaging and chemical analyses were performed using a double-corrected, monochromated FEI Themis Titan 60–300 operated in STEM mode at 300 kV using the ChemiSTEM technology [26,27] (X-FEG and Super-X detector). Additionally, high-angle annular dark-field (HAADF) STEM images were acquired using the TEAM 0.5 instrument at the National Center for Electron Microscopy facility in the Molecular Foundry (MF,

Berkeley).

## 3. Results

### 3.1. Microstructure

Rapid solidification results in a bimodal size distribution of faceted Pb nanoparticles dispersed within Al-Ga matrices, as it was reported for the AlPb composite [22] and turned out to be independent of the Ga content. Larger Pb inclusions with curved interfaces are generally found at grain boundaries and at the sample surface, while Pb nanoparticles in the grain interior are faceted displaying a Wulff-shape of truncated cube-octahedrons, having diameters from 5 nm to 200 nm in size. Such Pb nanoparticles exhibit a cube-on-cube orientation relationship to the Al-Ga matrix, independent of the amount of Ga added.

### 3.2. Calorimetry (DSC)

The melting and solidification transitions of different  $\text{Al}_{99-x}\text{Ga}_x\text{Pb}_1$  composites (with  $x = 0, 1, 3$  and  $6$ ) have been systematically investigated by differential scanning calorimetry (DSC). The results are shown in Fig. 1 and summarized in Table 2.

Without Ga, melting of the Pb nanoparticles occurs partially at the bulk melting temperature, indicated by a dashed line in Fig. 1, and partially at higher temperatures where three additional and overlapping peaks are detected. The melting signal extends over a range of 40 K. With increasing Ga content the superheating of Pb particles is reduced. Finally, at a Ga concentration of 6 at.%, the Pb melting signal is detected predominately in a single peak about 7 K below the bulk melting temperature.

Similar, upon cooling solidification occurs at monotonously reduced temperatures with increasing Ga content. The melting and solidification onset temperatures are plotted in Fig. 2 as a function of the Ga content. The melting onset is decreased by 7 K and the solidification onset temperature decreases by 102 K.

### 3.3. Chemical analyses (EDX)

EDX analyses were carried out on individual Pb nanoparticles for various Ga concentrations. The Pb nanoparticles were mostly oriented along the  $\langle 110 \rangle$ -zone axis of the fcc matrix Al and imaged using HAADF-STEM, see Figs. 3a and 4a (note: white dots are Moiré pattern due to the overlap of Al and Pb atomic columns in projection). Thus, 6 facets (four  $\{111\}$  and two  $\{100\}$  facets) are imaged in edge-on conditions. The results of the chemical analyses using a spot size of  $\sim 1$  Å, representing 3 and 6 at.% Ga, are shown in Fig. 3b–e and 4b–e. The chemical analyses reveal that Ga segregates at the particle–matrix hetero-interface (Figs. 3d and 4d). The Ga concentration has been traced in the form of profiles across the Pb nanoparticle (see boxed area in Figs. 3d and 4d). They show peaks in the Ga signal at the interfaces (Figs. 3e and 4e). The increment, which is defined as the difference between the Ga concentration in the matrix and the peak value at the interface, is determined to be  $\sim 3\%$  ( $2.6 \text{ at.}\% \pm 0.3\%$  on average for four Pb nanoparticles in Al-matrices with different Ga concentrations). It must be noted, that this evaluation does not take into account the projected thickness of embedded interfaces and the overlying/underlying matrix; thus, the absolute concentration at the interface is equal or higher than 2.6 at.%. However, all measurements were performed at areas as thin as possible and the evaluated Ga content at the interface is independent of the matrix concentration of Ga. The Ga-concentration level across the Pb nanoparticle is always higher on average than the surrounding matrix concentration due to the projected overlap of the other eight remaining Ga-enriched

**Table 1**  
Chemical composition of the  $\text{Al}_{98}\text{Ga}_1\text{Pb}_1$ ,  $\text{Al}_{96}\text{Ga}_3\text{Pb}_1$  and  $\text{Al}_{93}\text{Ga}_6\text{Pb}_1$  ribbons measured by energy dispersive X-ray application using an FEI Nova NanoSEM 230.

	$\text{Al}_{99}\text{Pb}_1$	$\text{Al}_{98}\text{Ga}_1\text{Pb}_1$	$\text{Al}_{96}\text{Ga}_3\text{Pb}_1$	$\text{Al}_{93}\text{Ga}_6\text{Pb}_1$
Al	$98.9 \pm 02$	$97.8 \pm 02$	$95.6 \pm 0.2$	$93.4 \pm 07$
Ga	–	$1.1 \pm 01$	$3.3 \pm 01$	$5.8 \pm 07$
Pb	$1.1 \pm 01$	$1.1 \pm 0.1$	$1.0 \pm 01$	$0.8 \pm 01$

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