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REPORT

On Equilibrium Ga Intergranular Films in Cr₂GaCZhengMing Sun^{a*}, Michel W. Barsoum^b, Yamei Zhang^c and Hitoshi Hashimoto^a^aNational Institute of Advanced Industrial Science and Technology (AIST), Nagoya, 463-8560 Japan;^bDepartment of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA;^cDepartment of Materials Science and Engineering, Southeast University, Nanjing, People's Republic of China

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The presence of equilibrium intergranular films (IGFs) in metallic systems has long been postulated; compelling evidence for this idea, however, is still lacking. Herein differential scanning calorimetry, in the -60°C to 70°C temperature range, on bulk and Cr₂GaC powders was carried out. A sharp endothermic trough, roughly 50°C below the melting point of bulk pure Ga, in the powdered samples was taken to be strong evidence for the presence of IGFs in the latter. The troughs for the sintered body were much more diffuse suggesting that in this case, a distribution of grain boundary thicknesses exists. A temperature dependent adsorption energy is postulated to explain the reversible extrusion and resorption of $100\text{ }\mu\text{m}$ thick Ga micro-pillars.

Keywords: Intergranular Films, Wetting, Whiskers, DSC

Introduction In 1999,[1] we reported that bulk samples of the layered ternary nitride Cr₂GaN were observed to extrude filaments of pure Ga at room temperature. This was ascribed to the de-intercalation of Ga from the basal planes of Cr₂GaN. Later, we observed the growth of In whiskers from Zr₂InC surfaces that we ascribed to the diffusion of oxygen along grain boundaries (GBs) with the resulting volume increase leading to the slow extrusion of the In whiskers by Coble creep.[2] More recently, we showed that the same mechanism can be used to explain the extrusion of Pb whiskers from commercial brasses at room temperature.[3,4] We also reported on the room temperature spontaneous growth of Ga nanoribbons from Cr₂GaC surfaces, which was assumed to be due to surface wetting of Ga, followed by its de-wetting.[5]

The existence of intergranular films (IGFs) in metallic systems has long been postulated. The idea of solid-state activated sintering, where a refractory metal powder magically densifies at temperatures in which no bulk liquids exist when a pinch of Ni is added to the powder, is but one example.[6] Decades later, and borrowing ideas from the surface science community, the idea of an equilibrium thickness film, premelting and prewetting where amorphous films form at temperatures lower than the bulk melting points of the liquid phase were introduced.[7]

And while evidence for premelting and prewetting and the concomitant existence of IGF at GBs exist, evidence for the idea of an equilibrium IGFs has to date and as far as we are aware, been totally lacking.

While IGFs have been observed in metallic, molecular and ceramic systems,[8,9] since both Ga and Cr₂GaC are metal-like conductors, we focus on metallic systems. The presence of GB structural transitions in metallic systems is indicated by measured discontinuities or abnormalities in macroscopic properties, such as GB diffusivities.[10,11]

The purpose of this letter is to report on our findings of the formation of very thin Ga IGFs between Cr₂GaC grains. Not only do we present compelling evidence for the formation of these *equilibrium* IGFs, but further show that they melt $\approx 50^{\circ}\text{C}$ below the melting point of bulk Ga.

Experimental Powders of Cr (99.9%, -250 mesh), C (99.7%, $\sim 5\text{ }\mu\text{m}$) and $\sim 3\text{ mm}$ Ga flakes were mixed for 24 h, and were placed in an alumina crucible and that was heated in a vacuum furnace (0.01 Pa) at 1000°C for 2 h. The synthesized powder was sintered using a pulse discharge sintering process in vacuum (20 min at 1200°C under an applied stress of 50 MPa). X-ray diffraction (XRD) spectra of the powders and sintered body (not

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shown) were quite comparable and showed Cr_2GaC to be the majority phase, with limited amount of free Ga which was not detectable by XRD. At 6.71 g/cm^3 , the density of the sintered sample was 99% of theoretical.

The thermal properties of the powders and sintered bodies, as well as pure Ga, were characterized by differential scanning calorimetry (DSC) in the -60°C to 70°C temperature range, at 10°C/min .

Results and Discussion Based on the DSC results for the pure Ga, the melting point was determined to be 28.7°C ; the specific heat of fusion was 79.2 J/g . These values compare well with literature results, viz. 29.78°C and 80.2 J/g . Based on scanning electron microscopic (SEM) micrographs of the sintered Cr_2GaC sample, (Figure 1), the grain size was found to range from a few to a few tens of micrometers.

Figure 2 shows two SEM micrographs, taken two hours apart, of a $\approx 100 \times 100 \mu\text{m}^2$ Ga micro-pillar that had sprouted from the Cr_2GaC surface, as it is slowly absorbed *back* into the sintered bulk. At $\approx 15 \mu\text{m/h}$, the resorption rate was not only high, but quite linear. Furthermore, the roots of these whiskers (Figure 3(a) and 3(b)) were quite shallow. SEM of surfaces fractured at 77 K (Figure 3(c)) showed the whiskers to be solid, i.e. not hollow.

Figure 4(a) compares the DSC results for the powders to those of the sintered sample and pure Ga upon heating. Based on these results it is obvious that (a) on heating, a clear, sharp, endothermic trough, centered $\approx -18.4^\circ\text{C}$, can be clearly seen for the powder. For the

sintered body, this trough is much smaller; (b) in both cases, a trough centered around 28.5°C is observed. The center of the trough for pure Ga is $\approx 35.8^\circ\text{C}$ and (c) on second heating of the powder, the area of the -18.4°C trough increases at the expense of the one at 28.5°C . Further cycling resulted in a slow but steady increase of the area of the -18.4°C trough at the expense of the one at 28.5°C (Figure 2(c)).

Figure 4(b) compares the DSC results for the powders to those of the sintered sample and pure Ga upon cooling. These results show that (a) for the sintered compound, an exothermic peak initiates at 16.3°C and extends to at least -44°C ; (b) for the powder, the exothermic peaks initiate around $\approx 16.3^\circ\text{C}$, but the majority of the heat is released around -28°C . On second cooling, outside a few new sharp peaks at -7.5°C , -44°C and -52°C , the overall shape of the DSC curve remains the same.

The resorption of the large extrudate with time (Figure 2) implies that the driving force responsible for its extrusion is reversible. It follows that the mechanism we proposed for the extrusion of low melting metals, viz. the diffusion of oxygen along the GBs [2] cannot be the operative mechanism here since the latter is irreversible. The relatively high linear rate and its rapidity further preclude diffusion as the operative mechanism. The only plausible mechanism remaining, therefore, is a wetting/de-wetting transition. In the remainder of this letter we make the case for this mechanism.

Before doing so it is useful to estimate the thickness of these IGFs. Assuming the grains to be cubes, $2 \mu\text{m}$ to

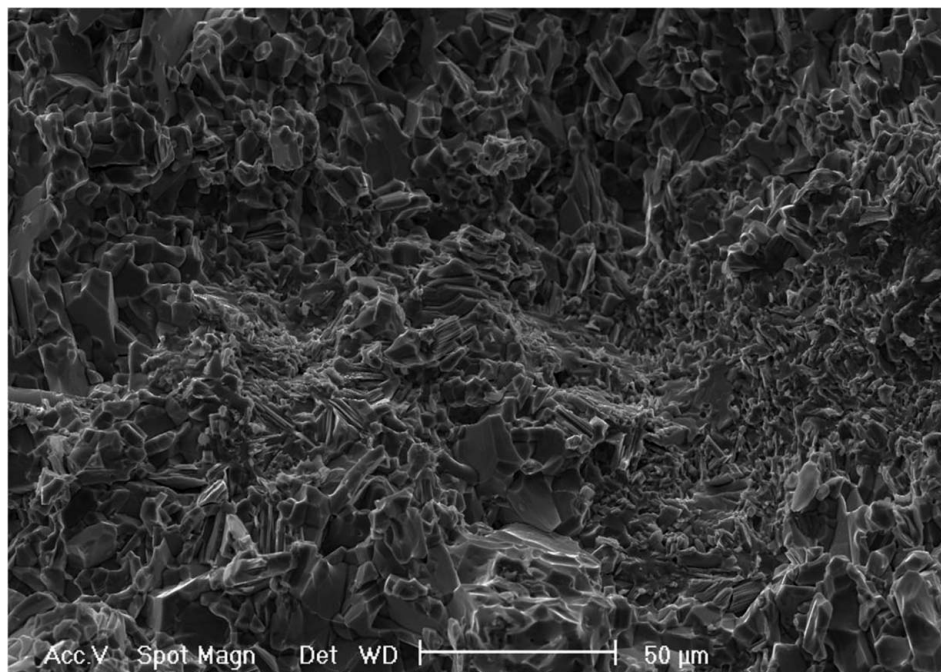


Figure 1. Fracture surface of a sintered Cr_2GaC showing the grain size ranging from a few micrometers to a few tens of micrometers.

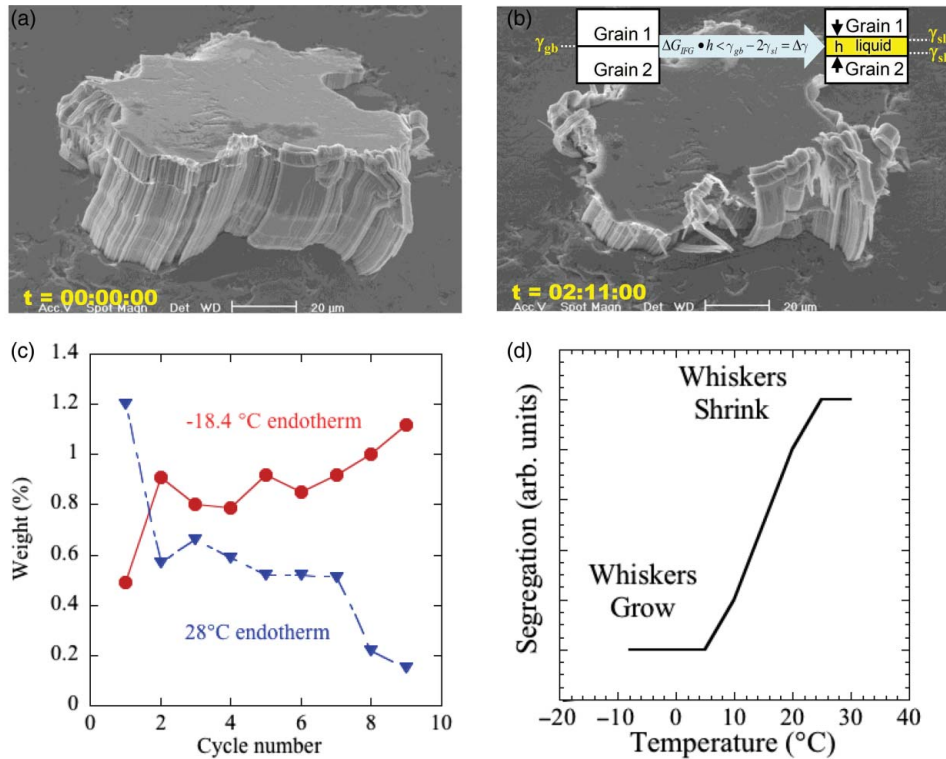


Figure 2. Time lapse SEM micrographs of a Ga micro-pillar as it is resorbed into the sintered matrix, (a) initially and (b) after ≈ 2 h. (c) Plots the areas of the endothermic troughs at -18.4°C and 28°C as a function of heating/cooling cycles. Inset in (b) is schematic of how a thin quasi-liquid layer can be stabilized at a GB. (d) Sketches the proposed absorption versus temperature relationship needed to explain the extrusion/resorption of the micro-pillars.

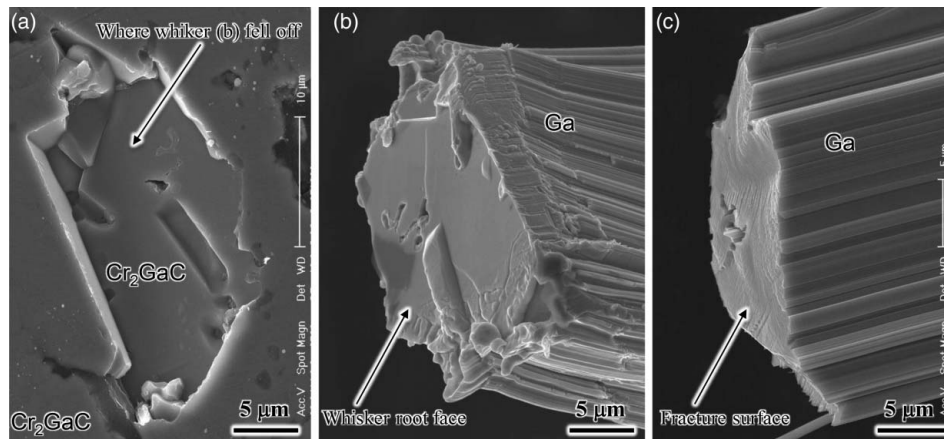


Figure 3. SEM micrographs of some features of a Ga whisker on the surface of Cr_2GaC sample: (a) the site of the whisker, which was removed and its root shown in (b), whereas (c) shows the fracture surface of the whisker which was fractured at the liquid nitrogen temperature.

a side, with a 2 nm thick Ga layer between them, represents a weight fraction of ≈ 0.26 wt.% Ga, a value that is roughly equal to that measured herein (Figure 2a). For the Ga micro-pillars to grow and shrink via a wetting/de-wetting transition a liquid must be present. The DSC results (Figure 4) present ample evidence for the presence of Ga liquid, in both the powder and sintered compacts.

The next question is: why under certain circumstances the liquid de-wets, while under nominally

identical conditions, the opposite occurs? To understand this intriguing phenomenon, one needs to invoke the existence of a temperature dependent GB segregation—centered around ambient temperature—shown schematically in Figure 2(d). Such transitions are well established in colloid chemistry.[12,13] During growth, liquid rejected from the GBs must flow from the interior to the root of the growing pillar. Once at the root, it solidifies and pushes the pillar outward. When the temperature is

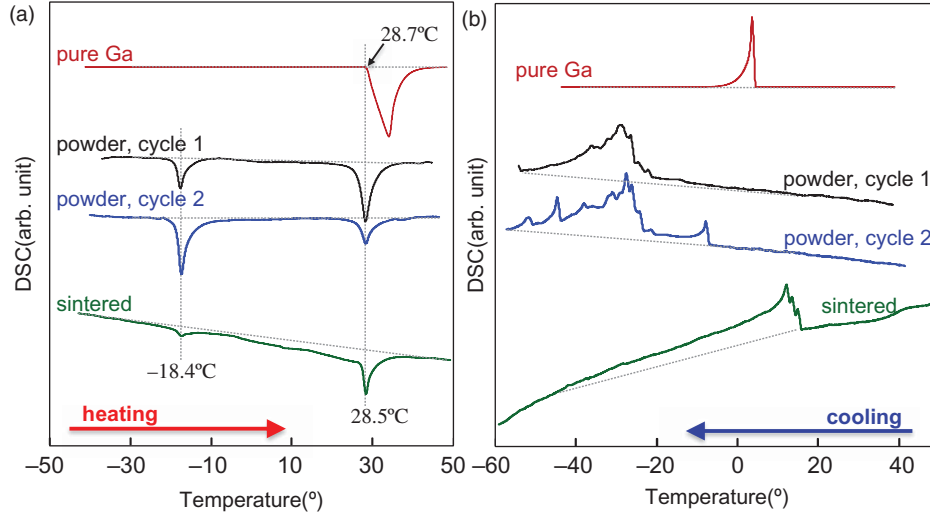


Figure 4. Summary of DSC of powders, sintered compacts and pure Ga upon, (a) heating and (b) cooling. The first and second heating and cooling runs for the powders are shown.

Note: All runs and their designations are color coordinated.

increased, the atoms at the root of the pillar *pre-melt* and flow back into the GBs, shrinking the pillar. The fact that the roots are shallow and of the same area as the micro-pillars (Figure 3(a) and 3(b)) is an important observation consistent with this notion. Premelting and prewetting are related, and thus the existence of both in the same system is not surprising.[9,12,13]

In addition to solving a somewhat baffling observation, the DSC results contain a plethora of other important information concerning IGFs and their behavior in metallic systems. Current understanding of impurity-based IGFs assumes they are amorphous. Based on the results shown in Figure 4, it is reasonable to assume that whatever films are present between the grains—at $< -18^\circ\text{C}$ for the powders, and $< 28.5^\circ\text{C}$ for the compacts—are most probably amorphous. The rapid growth and shrinkage of the Ga micro-pillars is also strong indication that a liquid is present.

Probably the most surprising and intriguing result is the sharpness of the endothermic peak at -18.4°C ; it is sharper than that of high purity Ga (Figure 4(a)). This result suggests that when they solidify, the IGFs may not be as disordered as generally assumed. This comment notwithstanding HRTEM is indicated and should be performed.

The sharp endotherm at -18.4°C , implies that the IGFs are, most probably, remarkably uniform in thickness. In other words, they are *equilibrium* IGFs. This is best evidenced by comparing the DSC response of the powders and sintered samples, as well as, the first and subsequent heating cycles for the powders. The simplest explanation for the difference is that the powders are free to adjust their separation to an equilibrium value; in the sintered body, the grains are not free to move to accommodate the Ga and, instead of a sharp peak at -18.4°C ,

the films melt over the much wider temperature range of -18°C to 30°C (Figure 4(a)).

This idea is corroborated by the fact that thermal cycling results in an *increase* in the areas of the endothermic troughs at -18.4°C at the expense of those at 28°C (Figure 2(c)). This observation is explained by assuming that the thermal cycling breaks up some of the agglomerates and allows more Ga to penetrate in between the latter. Another strong indication that the IGFs are equilibrium films is the presence, at all times, of excess Ga that melts at a temperature that is quite close to that of pure Ga (Figure 4(a)).

At an undercooling, ΔT , below T_{mp} , the Ga in the GBs melts. The IGF free energy is given by [14]:

$$\Delta G_{\text{IGF}} = \Delta H_f \left[\frac{\Delta T}{T_{\text{mp}}} \right], \quad (1)$$

where ΔH_f is the heat of fusion of pure Ga. The bulk penalty associated with the IGF formation is the replacement of the higher GB energy, γ_{gb} , by solid-liquid surfaces with energies, γ_{sl} (inset in Figure 2(b)). Wetting or penetration occurs when:

$$\Delta G_{\text{IGF}} \cdot h < \gamma_{\text{gb}} - 2\gamma_{\text{sl}} = \Delta\gamma, \quad (2)$$

where h is the thickness of the IGF. For a ΔT of 50°C , a $\Delta\gamma$ of $\approx 0.078 \text{ J/m}^2$ can account for a 1 nm thick pure Ga IGF. For a 10 nm film, a $\Delta\gamma \approx 0.8 \text{ J/m}^2$ would be required.

The fact that the IGFs solidify over a much wider temperature range than pure Ga (Figure 4(b)) is significant and consistent with the idea that the IGFs behave in a manner that is unlike bulk Ga. At $\approx 16.3^\circ\text{C}$, the Ga solidification peak onset for the sintered body is higher than that of pure Ga at $\approx 5^\circ\text{C}$, and significantly higher than those of the powders at $\approx -28^\circ\text{C}$. It is thus clearly more

difficult to solidify the *equilibrium* IGFs (in the powders) than it is IGFs between GBs—that solidify over the much wider 16.3 to $\approx -44^\circ\text{C}$ temperature range (top curve in Figure 4(b))—in the sintered body and/or pure Ga. Note that a fraction of the IGFs solidify at $\approx -60^\circ\text{C}$ (Figure 4(b)), some 90°C below T_{mp} of bulk Ga.

The response of the sintered solid, wherein the IGFs melt and solidify over a wide temperature range (Figure 4(a) and 4(b)) because of their wide distributions in thicknesses may be one reason clear, compelling evidence for equilibrium IGFs in metallic solids has to date been lacking. Our work suggests that it is more fruitful to work with powders to study this phenomenon.

Conclusions A DSC study on Cr_2GaC powders revealed a sharp endothermic trough roughly 50°C below the melting point of Ga. This was taken to strong evidence for the presence of IGFs. The reversible extrusion and resorption of Ga micro-pillars was observed on the Cr_2GaC surface of a sintered sample. The latter was interpreted to be due to a temperature dependent adsorption mechanism.

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