Transgranular liquation cracking of grains in the semi-solid state

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Grain refinement via semi-solid deformation is desired to obtain superior mechanical properties of cast components. Using quantitative \textit{in situ} synchrotron X-ray tomographic microscopy, we show an additional mechanism for the reduction of grain size, via liqation assisted transgranular cracking of semi-solid globular microstructures. Here we perform localized indentation of Al-15wt.%Cu globular microstructures, with an average grain size of \(\sim 480 \mu\text{m}\), at \(555 \degree\text{C}\) (74\% solid fraction). Although transgranular fracture has been observed in brittle materials, our results show transgranular fracture can also occur in metallic alloys in semi-solid state. This transgranular liqation cracking (TLC) occurs at very low contact stresses (between 1.1 and 38 MPa). With increasing strain, TLC continues to refine the size of the microstructure until the grain distribution reaches log-normal packing. The results demonstrate that this refinement, previously attributed to fragmentation of secondary arms by melt-shearing, is also controlled by an additional TLC mechanism.
A number of in situ experimental\textsuperscript{1–4} and modelling\textsuperscript{5} studies have recently reported how partially solidified metals can deform with the characteristics of a granular material\textsuperscript{6,25}; specifically, they form defects between the grains via pores/damage occurring in the intergranular liquid\textsuperscript{22–24}. However, a less-frequently reported observation in non-metallic semi-solid systems is transgranular cracking, which has been observed in low-temperature brittle metals\textsuperscript{19–22}, nano-crystals\textsuperscript{10}, graphene\textsuperscript{11} and other brittle materials (for example, glass beads\textsuperscript{12} and rocks\textsuperscript{13–15}). This failure mode has also been reported in a few high-temperature\textsuperscript{16,17}, using post-mortem analyses. Although there have been a few cases of transgranular failure reported in completely solid metals during fatigue at high temperature\textsuperscript{18}, such a mechanism has not been reported in semi-solid metals, where the primary (solid) phase is expected to be very ductile. Similarly, the process of liquefaction cracking, or cracking along the liquid channels between grains, also known as intergranular failure, is observed in heat affected zones during welding of aluminium alloys\textsuperscript{19}, austenitic steels\textsuperscript{20} and superalloys\textsuperscript{21}. However, it has not been reported to occur within grains, typically due to the lack of pre-existing liquid channels.

Semi-solid microstructural responses to the imposed deformation is important in advanced alloys because they are subject to deformation due to shrinkage forces and thermal contraction during conventional processing or when shear forces are applied\textsuperscript{26–28}. In these cases, a temperature window is encountered where solid grains and intergranular liquid coexist; that is, the material is semi-solid but capable of transmitting load\textsuperscript{25,26}. The microstructural response to these forces is known to strongly depend on the grain size and morphology of the material\textsuperscript{27}, which is important for thixoforming and other forming processes\textsuperscript{28,29}. The reduction in grain size during semi-solid processing has been primarily attributed to fragmentation of secondary arms\textsuperscript{25,30,31}. During shearing of semi-solid melts containing equiaxed dendrites, secondary arms detach from the primaries, and subsequently coarsen to form globular microstructures. This fragmentation process has been hypothesized to occur by formation of high-angle grain boundaries (large plastic deformations), and eventual detachment\textsuperscript{30}, in addition to remelting and pinch-off\textsuperscript{53,25}. Doherty et al.\textsuperscript{30} also hypothesize that these high-angle grain boundaries might be subjected to wetting, further reducing the energy required to break these secondary arms. Likewise in some brittle materials, such as rock salts and Cu-based alloys, transgranular cracking in single crystals has been accelerated by the presence of a liquid phase (saturated solution) inducing a stress-corrosion cracking-like mechanism\textsuperscript{14,33}.

In this study, we investigate the micro-mechanical response and failure mechanisms of a semi-solid granular material during indentation using in situ synchrotron X-ray tomography. Capturing the process at temperature allows us to quantify the motion, deformation and failure of large globular grains in a semi-solid alloy. Indentation of Al-15 wt.%Cu semi-solid globular microstructures was performed using fast high-resolution X-ray tomographic microscopy at the I12 beamline at the Diamond Light Source, UK\textsuperscript{34}. Although indentation is typically employed on solids, the purpose of using an indenter in this study was to obtain a localized deformation, preferably by pushing a single grain to perturb and stress the granular system.

Results

**In situ observation.** The in situ tomographic observations of indentation into a semi-solid alloy are shown in Fig. 1. The motion of the indenter (red, 2 μm s\(^{-1}\)) and granular flow of the solid α-Al grains (light grey) in the copper-enriched liquid (white) is captured at four time points (Fig. 1b–e; Supplementary Movie 1). Unlike any prior studies on semi-solids, these results capture the first instance of transgranular fracture of ductile grains (Fig. 1d, region of interest marked with a yellow circle). This is shown in three-dimension (3D) in Fig. 1g–j. At the beginning of the deformation (Fig. 1c,h), grains near the indenter show granular flow before being constrained by their neighbours. This is followed by significant cracking of the highlighted grains in the region of interest as well as those around the indenter (Fig. 1d,i). Several other grains undergo cracking on continued deformation as evident from the final scan at room temperature (Fig. 1e,j). Note that the cracks are liquid filled. The load steadily increases during indentation via a series of small jumps (Fig. 1f), most likely due to an increase in local densification of the solid with the load relaxing each time a grain fragments. Similar results were observed for other indenter displacement rates of 0.5 and 10 μm s\(^{-1}\), with prominent regions of cracking below the indenter (Supplementary Fig. 1).

The region of highly fractured grains is localized near the indenter with the grains in the bottom half only undergoing granular motion (2 μm s\(^{-1}\); Fig. 1e), suggesting that a localized force chain\textsuperscript{35,36} forms where a critical cracking stress is exceeded. Similarly, in the other two cases (Supplementary Fig. 1), the transgranular cracking is localized into a single constrained region. As grains crack, the fragments rearrange through granular flow accommodating the applied strain for a short time, until the fragments are pinned again, with contact stresses rising sufficiently to crack the grains into increasingly smaller fragments. This fragmentation causes localized densification of the solid phase, forcing liquid into the regions with lower load and no fragmentation. This is quantitatively compared in Fig. 1e where the yellow fragmented region has a solid fraction of 78% and the blue circled region has a solid fraction of 65%. Scanning electron microscopy and electron backscatter diffraction (EBSD) images of the initial microstructure and final cracked microstructure (Supplementary Fig. 2; Supplementary Note 1) clearly show transgranular fracture. Interestingly, even when examining such early works as those of Doherty et al.\textsuperscript{30} and Flemings\textsuperscript{25} on semi-solid deformation, similar features where a globular grain has split into two hemispherical halves can be observed; however, the present study is the first to provide an explanation for these features.

**Estimation of limiting contact stress.** Figure 2a shows one of the first fractured grains near the indenter tip (rendered in yellow) before cracking; its immediate contacting neighbours are coloured grey and their common contact areas are coloured red. After an indenter displacement of 144 μm, the grain cracks into two pieces (Fig. 2b, purple and pink). The observations in Figs 1 and 2 (Supplementary Figs 1 and 2) show that any grain in the sample can potentially crack if it is constrained and loaded. To estimate the contact stress responsible for cracking, we consider a layer (or bed) of constrained grains (within a volume of an average grain’s height), to which the applied load is transmitted (shown schematically in Supplementary Fig. 3). Let \( F \) be the load from the indenter (transmitted to any single grain within a constrained layer) linked through a force chain. The areas normal to the applied load (marked in blue in Supplementary Fig. 3) are likely to transfer the load directly. An estimate of stress transmitted through these normal areas is given by \( \sigma_{\text{est}} = \frac{F}{\sum_{i=1}^{n} A_i} \).

We can bound this estimate with a lower bound stress, calculated by assuming \( F \) is transmitted through all possible contact areas, with \( \sigma_{\text{lower}} = \frac{F}{\sum_{i=1}^{n} A_i} \), and an upper bound using just a single contact\textsuperscript{12}, \( \sigma_{\text{upper}} = \frac{F}{A_i} \). The contact areas were calculated directly
Figure 1 | Semi-solid indentation of globular microstructures. (a) schematic of the set-up, (b–d) sequence of 2D longitudinal slices, with the indenter coloured red, showing the onset and development of transgranular cracking of globular microstructures at 555 °C during indentation with a speed of 2 μm s⁻¹ (corresponding to the instances marked in f). (e) The final room temperature scan. (f) The load measurement (averaged). (g–j) The corresponding 3D sectional views of segmented solid grains (coloured by size). I denotes the corresponding indenter position. The yellow dashed circles in b–e and the black circles in g and h highlight region of interest where transgranular fracture of seemingly ductile grains is occurring. The blue circle indicates the region of apparent increase in liquid after indentation. Scale bar, 500 μm.

Figure 2 | 3D visualization of transgranular liquation cracking. 3D rendering of a grain (shown inside the black circle in Fig. 1g–h) cracking into two during indentation: (a) initial arrangement at I = 0 μm with the contact areas in the field of view coloured red and (b) cracked morphology at I = 144 μm. Scale bar, 200 μm.

Figure 3 | Log-normal distribution of cracked grains. (a) Grain size distribution of initial and final Al–Cu microstructures after semi-solid indentation at various indentation speeds (units: μm s⁻¹). 3D rendering of solid grains, coloured by size, at (b) the initial state for the 0.5 μm s⁻¹ indentation speed and at the final states for the (c) 0.5, (d) 2 and (e) 10 μm s⁻¹ indentation speeds, respectively. Scale bar, 750 μm.

**Grain size distribution.** The initial grain size distribution for the 2 μm s⁻¹ case is plotted in Fig. 3a (note the initial distribution of grains is near identical for all samples since they were all machined from one starting block), together with the final size distribution at the end of the indentation sequence for the three indenter velocities. Interestingly, for all speeds, indentation causes the grains to fracture such that they form log-normal distributions. Such a log-normal particle distribution is one of the optimal distributions for obtaining maximum packing density. This implies that the system is responding to the imposed deformation by naturally increasing its packing density to best distribute the load. The 3D sectional views of the final microstructures at indenter displacement rates of 0.5 and 10 μm s⁻¹ (Fig. 3c,e, respectively) show that the localized force chain and associated cracking occurred directly below the indenter. In all cases, the mode of the grain size halves on deformation, and the number of grains doubles (as listed in Table 1), but the greatest cracking and size reduction happens at
Table 1 | Comparison of cracking data for different deformation speeds.

<table>
<thead>
<tr>
<th>Indentation</th>
<th>Speed (μm s⁻¹)</th>
<th>Depth (mm)</th>
<th>Solid fraction (%) (at 555 °C)</th>
<th>Number of grains</th>
<th>Drain diameter (μm)</th>
<th>Number of grains</th>
<th>Grain diameter (μm)</th>
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<tbody>
<tr>
<td></td>
<td>Before indentation</td>
<td></td>
<td>After indentation</td>
<td></td>
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<tr>
<td></td>
<td>Mean</td>
<td>s.d.</td>
<td>Mode</td>
<td>s.d. (log-normal)</td>
<td>Mean</td>
<td>s.d.</td>
<td>Mode</td>
</tr>
<tr>
<td>0.5</td>
<td>0.8</td>
<td>73.7 ± 2</td>
<td>159</td>
<td>484</td>
<td>234</td>
<td>383</td>
<td>380</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>73.4 ± 2</td>
<td>162</td>
<td>489</td>
<td>253</td>
<td>511</td>
<td>205</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>73.5 ± 2</td>
<td>168</td>
<td>481</td>
<td>226</td>
<td>364</td>
<td>295</td>
</tr>
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2 μm s⁻¹ (Fig. 3d), where the first force chain forms to the sidewall. This observation confirms the stochastic behaviour of granular flow, even when constrained and subject to transgranular failure. It is important to note that these measurements are limited by the pixel size (4 μm per pixel) of the imaging setup from I12 used in this study, whilst scanning electron microscopy images show cracks and liquid films that have thicknesses less than this³⁹ (Supplementary Fig. 2).

Role of solid volume fraction. To determine the dependence of cracking on the amount of liquid between grains, indentation experiments were performed at a higher temperature (570 ± 5 °C) with a speed of 0.5 μm s⁻¹, where the solid volume fraction was 62 ± 2% (as compared with 73% fraction solid for the previous experiments). With the increased liquid fraction (from 27% to almost 40%), no cracking was observed; see Fig. 4 and Supplementary Table 1 for further experimental details. Much more granular motion can be observed, with the grains freely translating and rotating to accommodate deformation⁴. From this data, it appears that the propensity of cracking is directly influenced by the solid volume fraction. This is also consistent with the observations shown in Fig. 1e, where increased packing in the fragmented region was observed. Furthermore, the occurrence of cracking is independent of the indenter shape (Supplementary Fig. 4) and the deformation rate within the observed range of deformation speeds (0.5–10 μm s⁻¹). Hence, we can hypothesise that there is a minimum solid fraction above which the grains contact sufficiently to form force chains that constrain motion, and this leads to transgranular fracture.

Discussion

These experimental findings pose important questions about how and why transgranular cracking can occur so readily in the single-crystal primary phase (α-Al) globular grains of an alloy in the semi-solid state. Prior studies have only reported cracking (and other defects such as damage voids) to occur between grains, or intergranularly¹–⁷. Further, liquidation cracking during welding²⁰ and liquid metal embrittlement⁴⁰ are also assumed to occur intergranularly. This is the first time transgranular liquidation cracking (TLC) has been observed in situ and quantified in semi-solid alloys, similar to transgranular cracking in brittle materials.

On the basis of the experimental observations, we hypothesize that the cracking happens via a combination of mechanisms in a series of stages, shown schematically in Fig. 5a–d. As a semi-solid globular alloy is compressed under constraint and the fraction of liquid is low, intergranular liquid will flow to regions of lower pressure²,²²,²³,⁴¹ and grains will contact each other forming a force chain. Note that each grain is a near-perfect single crystal but has a random crystallographic orientation (Fig. 5a; Supplementary Fig. 2). Once the grains become pinned, they will apply compressive and shear loads at a range of misorientations depending on the orientation of the grain. A number of neighbours will apply small but multiple contacts around the primary α-grain (Fig. 5b). This leads to localized elastic and small plastic strains (Fig. 5c), generating dislocations that move to the surface quickly (dislocation mobility increases at elevated temperatures). The dislocations are likely to pin and interlock, as well as cause roughness at the surface and a localized increase in free energy, which results in localized remelting. The intergranular liquid is then drawn into the crack, causing TLC (Fig. 5d). Note that the coarsening process can lead to an occasional formation of small liquid pockets²⁵ (< 10 μm size), which act as potential stress concentrators deflecting the crack (curved crack in Supplementary Fig. 2b). Similar to stress- and liquid-assisted cracking of rock salts and Cu-based alloys, the
interdendritic liquid surrounding these grains acts as an interface destabiliser, inducing a stress-corrosion type acceleration of the crack (compressive stresses required for fracture range from 3 to 100 MPa (refs 14,43)). The proposed mechanism can also be correlated to fragmentation of secondary arms during melt shearing25,30, where forced melt flow induces large plastic deformation, causing remelting25 and wetting24-assisted detachment. We also see that the cracking occurs recursively (Supplementary Fig. 4) until no further contacts with required stress levels remain, that is, a log-normal distribution in grain size is reached.

The four stages during T/LC are therefore hypothesized (Fig. 5): motion and pinning of grains resulting in compressive and shear loads (Fig. 5a); dislocation generation, leading to surface perturbations and internal preferential crack paths34 (Fig. 5b); remelting25,32 at the surface perturbation45 (Fig. 5c); and crack growth from the surface of the grain accelerated by liquation (Fig. 5d). Although drawn schematically in Fig. 5a–d, we observe these same stages in our experiments, as shown in Fig. 5e–h from a zoomed-in region circled in Fig. 1b–e, clearly demonstrating the power of in situ synchrotron experiments to inform and quantify new mechanisms.

In summary, using in situ synchrotron X-ray tomographic microscopy, we have shown for the first time that, in addition to known fragmentation mechanisms, T/LC of grains contributes to grain size reduction in semi-solid alloys with high solid volume fractions. Localized deformation comparable to an average grain size on a constrained specimen is found to initiate cracks. Furthermore, liquation is observed to assist the propagation of cracks and the eventual granular separation. This fragmentation of primary γ-grains leads to final microstructures with log-normal size distributions, providing the highest packing density and optimal load distributions for the microstructures. The study has presented a quantified hypothesis of a new mechanism to achieve grain refinement that is relevant to materials processing, magmatic flows and oil/mineral extraction.

Methods
Thermomechanical setup. A bespoke thermal-mechanical setup was used to perform the semi-solid indentation. The apparatus consisted of a mechanical testing rig (P2R)1,2,46 and a loop-feedback controlled resistance furnace with an X-ray transparent window1,2,47. The samples were previously prepared by heat-treatment in a bespoke thermal-mechanical setup used to test a stressed solid/liquid interface. Geol. Soc. 200, 71–83 (2002).

Synchrotron experiments to inform and quantify new mechanisms.

Data acquisition and image processing. During the experiment at the I12 beamline of Diamond Light Source, 2 sets of 9 tomographic scans at 9-s intervals were acquired, with a 5-min interval in between each set of scans to offload the data from the camera. Each scan consisted of 900 projections, acquired using a 53-keV monochromatic X-ray beam. The camera consisted of a single-crystal cadmium tungstate scintillator, lens coupled with a Vision Research Miro 310M camera, giving a 4-μm pixel size. Each 3D scan was reconstructed using filtered back-projection to produce a 1,200 × 1,200 × 800 voxel volume per scan. Each 3D volume was filtered with median and anisotropic diffusion filters to reduce the noise, and then solid grains were segmented using a watershed-separation algorithm in Avizo (FEI VSG, France).

References