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Mechanical behaviour of rapidly solidified Copper – *effects of undercooling and strain rate*

by

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Abstract

In this paper we present the results, from what we believe is the first ever attempt to study the mechanical behaviour of pure Cu specimens, obtained by solidification of highly undercooled melts, at different rates of strain. Cylindrical compression specimens were successfully manufactured and tested from the as-solidified samples. The experimental results revealed that the strength of the studied system increases not only with an increase of the level of undercooling, but also with the rate of testing. Further microstructural analysis revealed that at undercoolings above 200K the Cu specimens underwent a transition from dendritic to a grain refined structure, which was accompanied with a break in the stress-undercooling relationship. It is suggested that on this occasion the transition was the result of two competing mechanisms: dendrite fragmentation and recrystallization. This is supported by extensive microstructural analysis using different microscopy techniques and Electron Back Scatter Diffraction. Finally, the relationship between the resultant grain sizes and measured stresses is compared against the Hall-Petch Law.

Keywords: undercooling, high strain rate testing, mechanical behaviour, copper

Introduction

For many years, containerless processing of metals and alloys has been successfully used as means to study the fundamentals of solidification, including processes, such as nucleation and growth [1, 2]. The techniques are based on avoiding sites for heterogeneous nucleation, such as crucible walls and impurities, which allow the molten material to be significantly undercooled below its melting point and maintained in this metastable state for prolonged periods of time. Once nucleation is triggered, a large driving force, caused by the large difference in Gibbs free energy between the solid and liquid states, leads to rapid solidification, resulting in non-equilibrium structures, such as dendrite deformation and grain refinement [3]. The main advantage of these methods, which include melt fluxing, drop tube processing and the levitation techniques, is that they allow direct monitoring and processing of bulk specimens, which enables further investigations of the mechanical behaviour of the studied material systems and their respective microstructures.

A number of authors have previously studied the undercooling behaviour and microstructural evolution of pure Cu, which was also the subject of this research. A brief summary of their findings is provided in the section below. The rationale for using a pure material is such that it limits the number of mechanisms that can impact the resultant mechanical properties; e.g. solid solution strengthening (via solute trapping at high growth velocities) is absent, as is any precipitate strengthening. In the earlier studies, Turnbull [4], Scheil and Fehling [5] were unable to observe any microstructural changes, such as grain refinement, at undercooling of up to 229 K. However, Powell [6] and later Kobayashi and Shingu [7] reported a transition from a coarse columnar to fine grained equiaxed structure in Cu containing small amounts of oxygen, at undercoolings above 150 K. In 1989, Willnecker [8] undercooled pure copper by 266 K prior to nucleation, but no evidence of grain refined structures was reported. Further studies by Costa

Agra Mello and Kiminami [9] and Li et al. [10] demonstrated that grain refinement in Cu occurs at undercoolings in the region of 270 - 320 K. It was suggested that the observed equiaxed microstructure arose from dendrite break up and it was further suggested that even higher undercoolings can be achieved with the use of higher purity starting material. Battersby et al. [11] studied the velocity–undercooling–microstructure relationship in pure Cu and Cu–O alloy at undercoolings of up to 250 K. For the case of pure copper, the authors reported that the growth velocity increased smoothly, but no evidence of grain refinement was found in any of the as-solidified samples. However, for the case of the Cu–O alloy, two grain refinement transitions were found at both low and high undercoolings and a break in the velocity – undercooling relationship was reported at high undercoolings. Interestingly, for both transitions the microstructural observations revealed that dendrite fragmentation appeared to be the governing mechanism. Finally, Dragnevski et al. [12, 13] reported undercoolings in pure Cu of up to 366 K. At undercoolings above 280 K the authors observed a transition from dendritic to seaweed morphology, and at extremely high levels of melt undercooling ($\Delta T \geq 352$ K) grain refined microstructures were observed. Microscopy and pole figure plots provided conclusive evidence that the grain refinement observed in pure Cu occurs via recrystallisation. This was further supported by microhardness data, which showed a significant reduction in hardness in the specimens undercooled above 350 K.

While there are no previous attempts to study the mechanical properties of Cu specimens, solidified from highly undercooled melts, apart from, as suggested above, some microhardness data [13], the behaviour of conventionally cast and heat treated pure Cu has been extensively studied in the literature as a function of grain size, temperature and strain rate [14, 15, 16] and it has been clearly demonstrated that the flow stress is grain size dependent and follows the well-known Hall-Petch equation [17, 18]:

$$\boldsymbol{\sigma = \sigma_0 + kd^{-x}}$$

where $\boldsymbol{\sigma}$ is the stress of a polycrystal, $\boldsymbol{\sigma_0}$ is the representation of the stress of a single crystal, $\mathbf{k}$ is a constant, $\mathbf{d}$ is the average grain size and $\mathbf{x}$ is a strain rate dependent constant usually between 0.5 and 1.0. From this, it is obvious that the strength of the specimen will increase with decreasing grain size. This has been proven experimentally to occur on a micron scale, but as some research has shown not necessarily on a nano-scale [19]. In 2013, Siviour et al. published an extensive review on the strain-rate dependency of pure Cu, where various interpretations for the increase of flow stress with strain rate based on dislocation models are considered [20]. Further comparisons of different sets of experimental data were also carried out in an attempt to understand the differences of the results obtained from essentially the same material. Some of the following were discussed: material grain size, experimental sources of error, including specimen dimensions and loading systems used. However, it was thought that the major contribution to the variation of the experimental results is the starting structure of the specimens. This is undoubtedly quite likely as even small differences in the processing route, e.g. heat treatment parameters, can have a significant effect on the mechanical response.

In this study, a melt encasement fluxing technique was used to produce Cu specimens at various levels of undercooling to study their mechanical behaviour at different rates of strain. Further microstructural analysis, including Optical Microscopy, Scanning Electron Microscopy and Electron Back Scatter Diffraction (Pole Figure Plots), provided additional information of how the microstructure affects the properties of the system under investigation. It is believed that the experimental results presented and discussed in this research represent the first attempt to utilise this approach to material systems obtained from bulk undercooling.

Experimental Methods

Melt fluxing was used to produce the Cu specimens (99.9999% purity ALFA Johnson Matthey) used for this study. As already demonstrated in the section above, this method allows high undercoolings to be achieved, mainly because nucleation on container walls is prevented and the glass flux also aids the removal of impurities from the melt and protects the surface from oxidation. The undercooling experiments were carried out in the Institute for Materials Research, University of Leeds, following a well-established and documented procedure, details for which can be found in our previous work [11, 12, 13]. A schematic diagram of the fluxing apparatus and the copper specimens is shown in **Figure 1**.

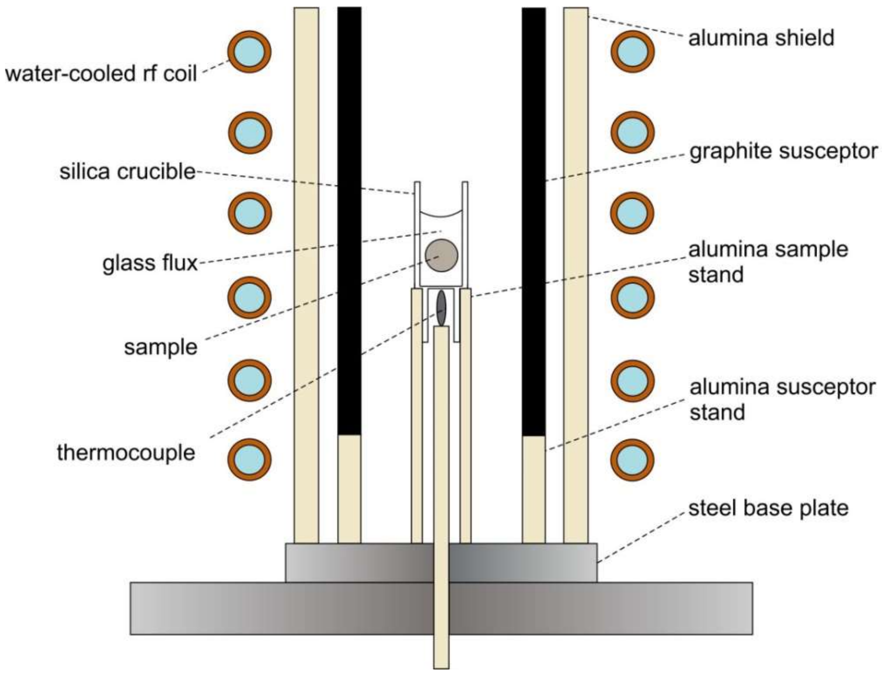


Figure 1 Schematic diagram of the fluxing furnace used to produce a range of rapidly solidified Cu samples, from various levels of melt undercooling.

By using this methodology, it was possible to generate a number of specimens form a large range of undercoolings, between 25 K and 215 K. The specimens, with spherical shape, were extracted from the crucibles and cleaned from any residue from the glass flux. Due to the size of the specimens, approximate dimensions 5 x 5 mm, it was only possible to manufacture specimens suitable for compression testing. These were made by turning the spherical material into small cylinders with dimensions' d = 4.45 mm and l = 2.55 mm, where d and l are diameter and length respectively. The compressive mechanical tests were carried out at 2 distinct rates of strain, here defined as Quasistatic and High, in an attempt to investigate any rate dependency in the material response as a function of undercooling. The quasistatic tests were performed on a commercial uniaxial Hounsfield testing machine equipped with a calibrated 10kN load cell. All quasi static experiments were performed at strain rates in the region of 1×10^{-3} s^{-1}. The high strain rate experiments were performed on an in house built split-Hopkinson pressure bar (**Figure 2**), controlled striker velocity, v ≈ 15 m/s). Calibrated strain gauges on the loading bars were used for obtaining both the resisting force and specimen extension; the loading rig is also equipped with a SIMX16 ultra high speed camera. The deformation of all the tested specimens was evaluated using the commercially available full field Digital Image Correlation software GOM Aramis.

For the microstructural analysis solidified specimens from different levels of undercooling were first mounted using Bakelite in a conventional hot mounting press. These were then ground down using 180, 400, 600 and 1200 grit Silicon Carbide media and then polished using 9, 3, and 1 micron water based diamond suspension. For the EBSD mapping further polishing using 0.25 micron colloidal silica was required. The Optical Microscopy was carried out on an Alicona G4 3-D Profilometer, equipped with a polarizer and a range of objective lenses. The Scanning Electron Microscopy (SEM) and Electron Back Scatter Diffraction (EBSD) analysis was done on a Carl Zeiss Evo LS15 instrument, equipped with various imaging detectors and an EDAX EBSD Hikari 4 Camera. Etching, to further reveal structure and sub-structure was done using Iron Chloride solution.

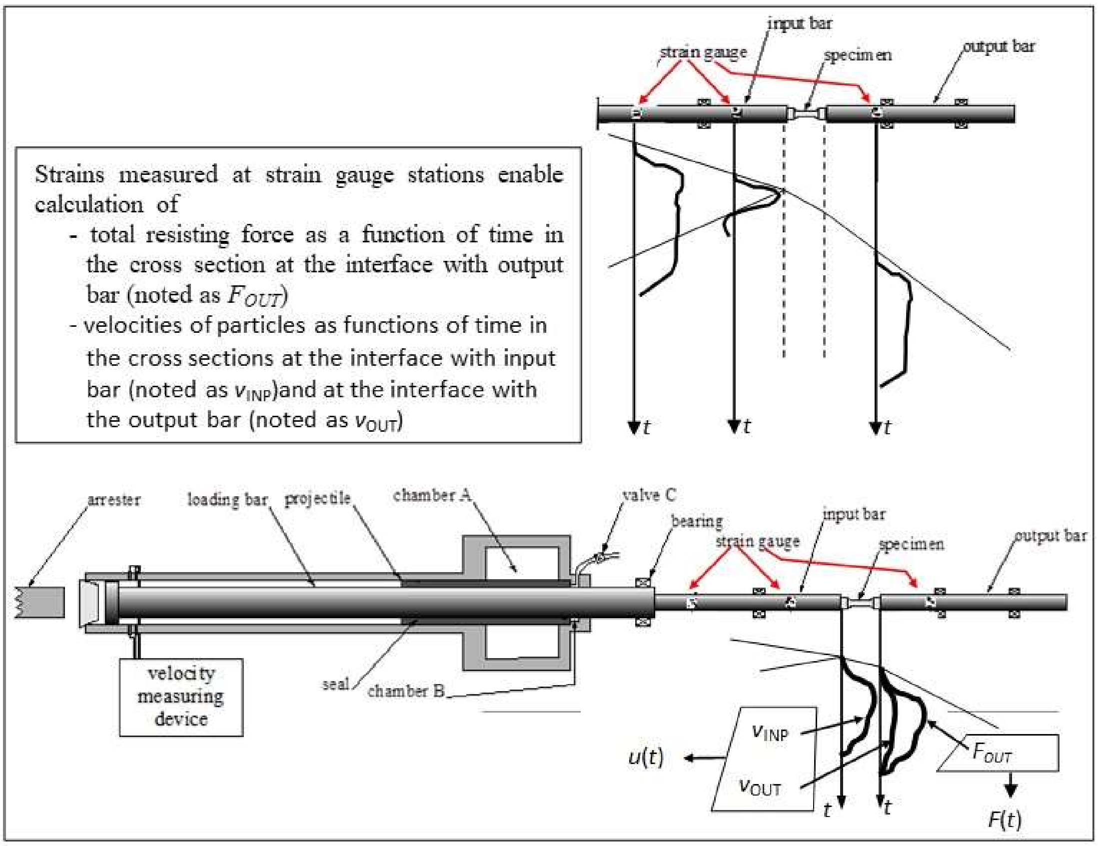
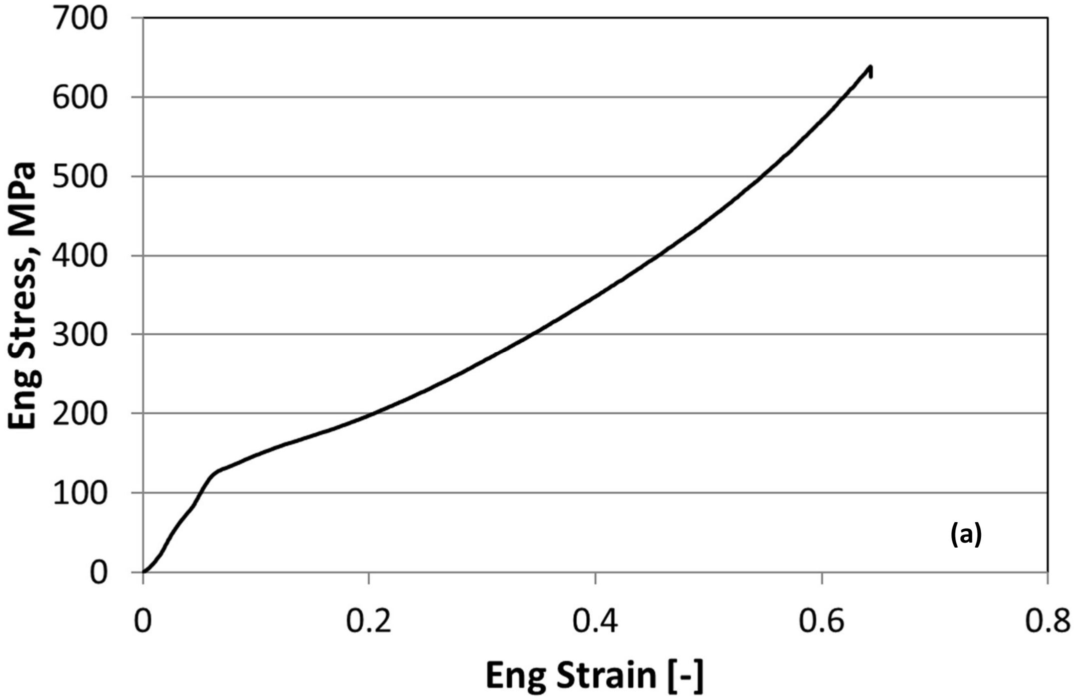


Figure 2 Schematic diagram of the Hopkinson bar set up for High Rate compression testing.

Results & Discussion

Mechanical response

Examples from the typical stress-strain curves obtained from the quasistatic and high rate compression experiments carried out on the solidified Cu specimens are presented in graphical format in **Figure 3** and the full dataset of measured stresses is presented in **Table 1**. Here it is worth noting that 25 K is a sufficiently small undercooling and hence it can be considered that the material is exhibiting equilibrium behaviour.



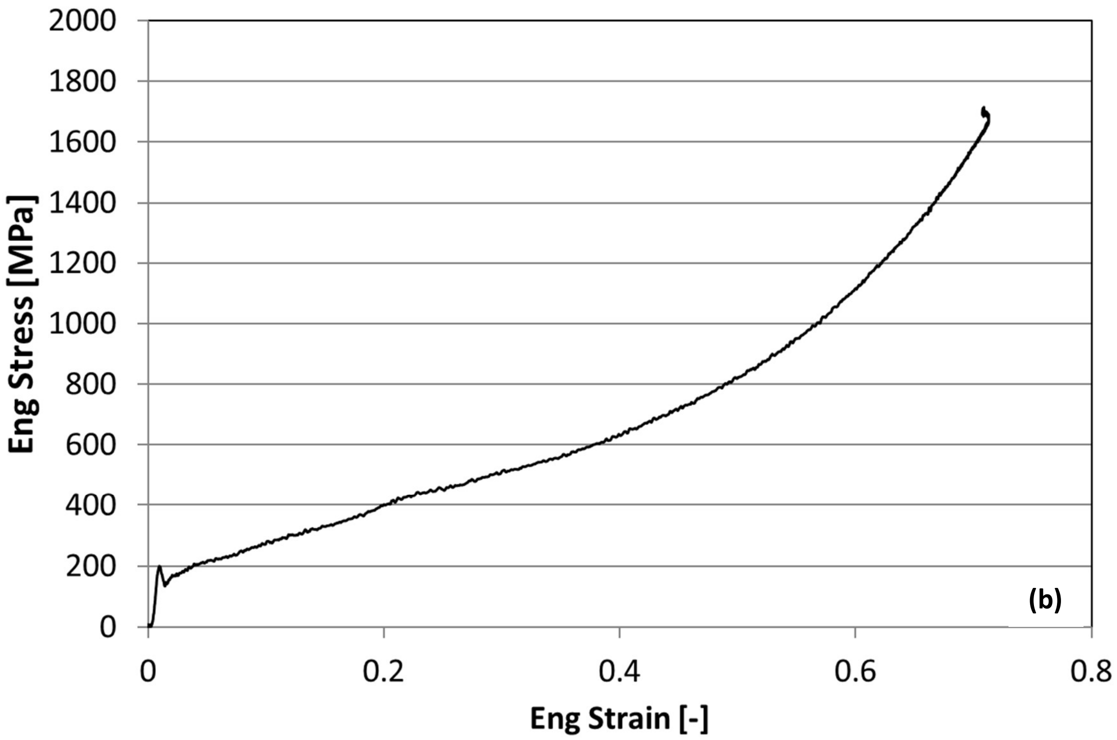


Figure 3 Example Engineering Stress vs Engineering Strain plots for undercooled Cu specimens obtained at quasistatic (a) and high (b) rates of strain.

From the data presented above it can be clearly seen that under quasistatic conditions the undercooled Cu specimens do not fail and after yielding the material continues to deform, with the specimen ending up in the shape of what is commonly referred to as a ‘pancake’. It is also evident that the level of undercooling does have an effect on the mechanical properties of the material; the Cu specimens tested at low undercoolings (<100K), yield at stresses in the region of 115 to 120MPa, whereas the values for the highly undercooled specimens are in the region of 140MPa.

Compression data for undercooled pure Cu specimens		
Undercooling, K	**Rate**	**Engineering Stress, MPa**
25	QS	116
50	QS	118
108	QS	119
136	QS	121
190	QS	125
209	QS	137
215	QS	139
86	HR	202
98	HR	201.5
119	HR	204
127	HR	205
207	HR	212
212	HR	216
212	HR	215.7

Table 1 Undercooling vs Engineering Stress for pure Cu specimens tested at quasistatic (QS) and high rates (HR) of strain

At high strain rates the Cu specimens exhibit similar mechanical behaviour; i.e. they do not fail and after yielding the material continues to deform. A sequence of images demonstrating the deformation behaviour of specimens during high rate testing obtained using a high speed camera is shown in **Figure 4**. However, here it is also clearly seen from the data in **Table 1** and **Figure 5** that the specimens yielded at much higher compressive stresses in the region of 200 to 220 MPa, thus suggesting that the mechanical properties of the rapidly solidified Cu specimens also depend on the rate of testing. The significant increase in strength measured at high rates of strain can be associated with an increase in dislocation density caused by the high impact velocities [20]. This seems to be the case for a wide range of undercoolings, between 80 and 200 K. Furthermore, it is also evident that the yield strength of the specimens undercooled by less than 100 K is noticeably lower than the yield stress for the specimens undercooled by more than 200 K prior to nucleation, which is suggesting that the level undercooling has an effect on the mechanical properties of the material. Hardness data obtained from previous studies on undercooled Cu specimens supports this trend [13].

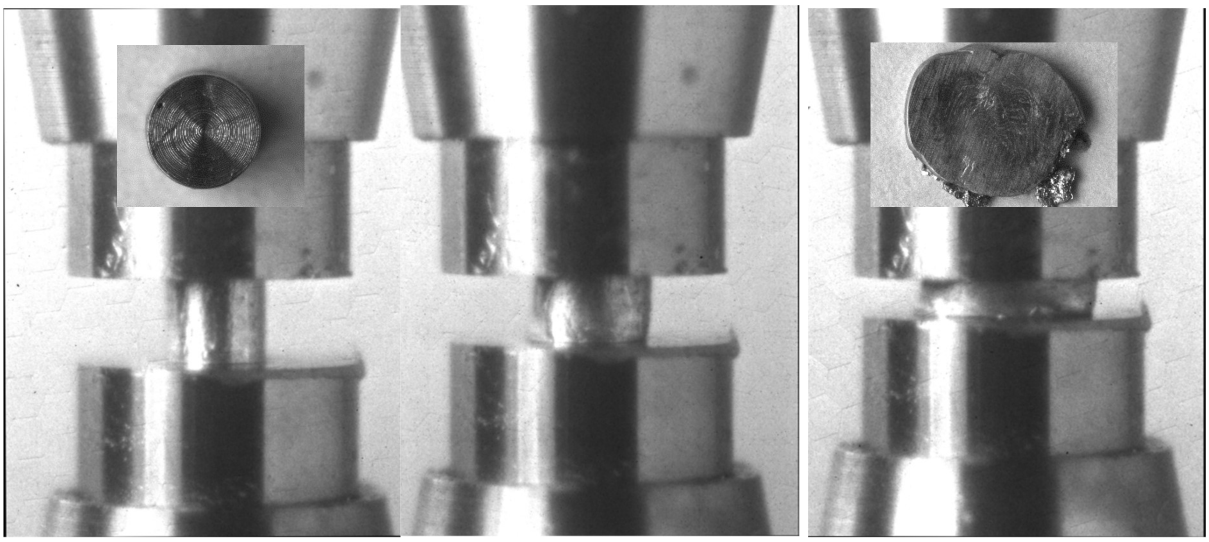


Figure 4 Example images obtained using the SIMX16 High Speed camera during a high rate compression test of a Cu specimen obtained by solidification from highly undercooled liquid. Insert top left – cross-sectional image of the specimen before loading, showing its circular shape; Insert top right – cross-sectional image of the specimen after loading demonstrating a change in shape from circular to oval.

From the images in **Figure 4** (inserts top left and right) it can also be seen that during the high rate experiments the shape of the initially cylindrical specimen changes from circular to oval, i.e. normal to the cylinder axis. A degree of barrelling, due to friction between the anvils and the specimen is to be expected during compression testing, although this appears to be rather small. Therefore, it is not unreasonable to suggest that the properties of the solidified specimens may differ depending on the direction of testing or specimen manufacture. In our study the cylindrical samples were manufactured along the growth direction. Hence, taking into account the way the specimens were cast, i.e. by means of triggering, which in essence induces directional solidification, some anisotropy in the mechanical properties is to be expected.

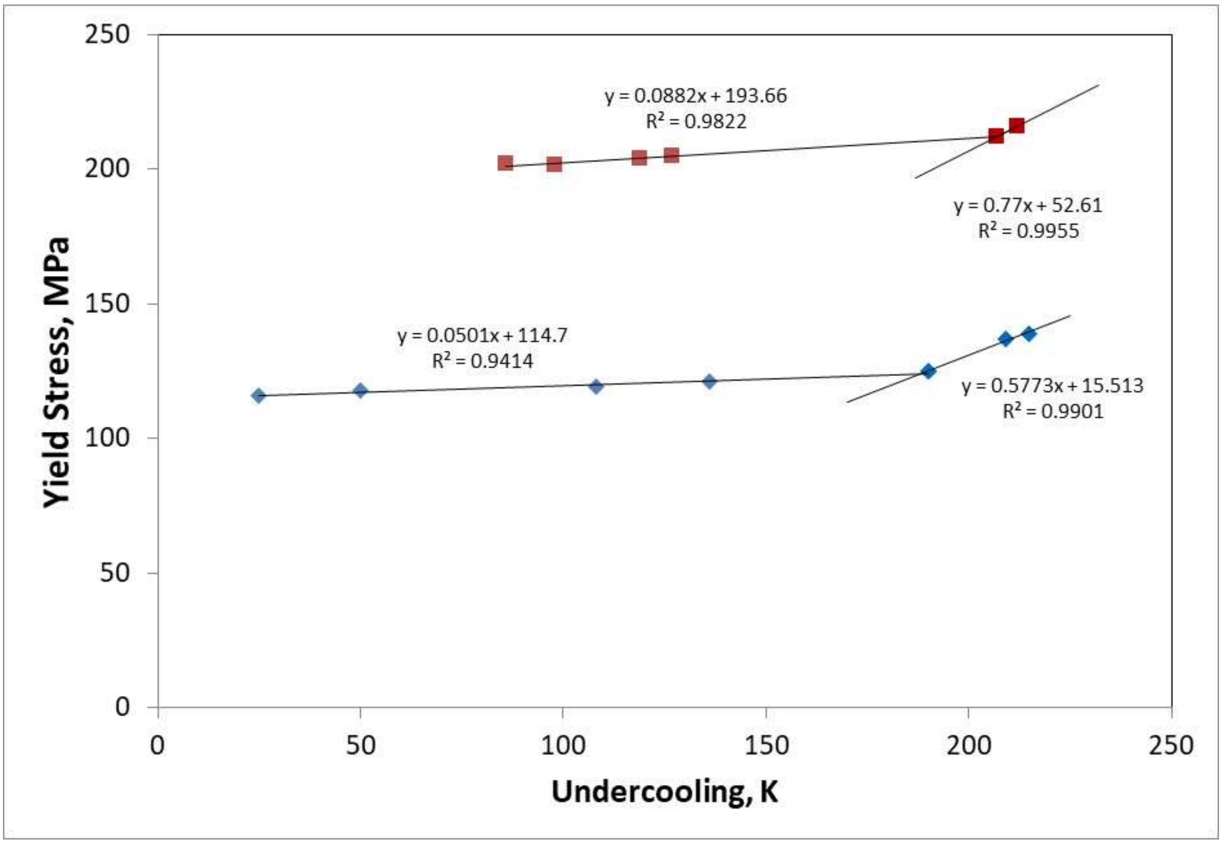


Figure 5 Yield stress for Pu Cu specimens at low and high undercoolings.

Finally, a closer look at the trends displayed in **Figure 5** indicate what appears to be a break in the stress-undercooling relationship at undercoolings of around 200K. To demonstrate this better, the two datasets were split into further two, one for undercoolings up to 200K and one for undercoolings above 200K. By adding and extrapolating linear trend lines to the individual datasets, the break becomes quite apparent. This is quite interesting, as abrupt changes in the behaviour of rapidly solidified specimens could be indicative of changes in the resultant microstructures. This is investigated further in the section below.

Microstructural observations

Figure 6 depicts the typical microstructure observed in specimens solidified from low undercoolings. At these levels solidification, in some cases, resulted in single grain growth (as in the example below) with reasonably well-defined dendritic structure. In other cases, coarse-grained structures were observed, which is consistent with previous observations [12, 13].

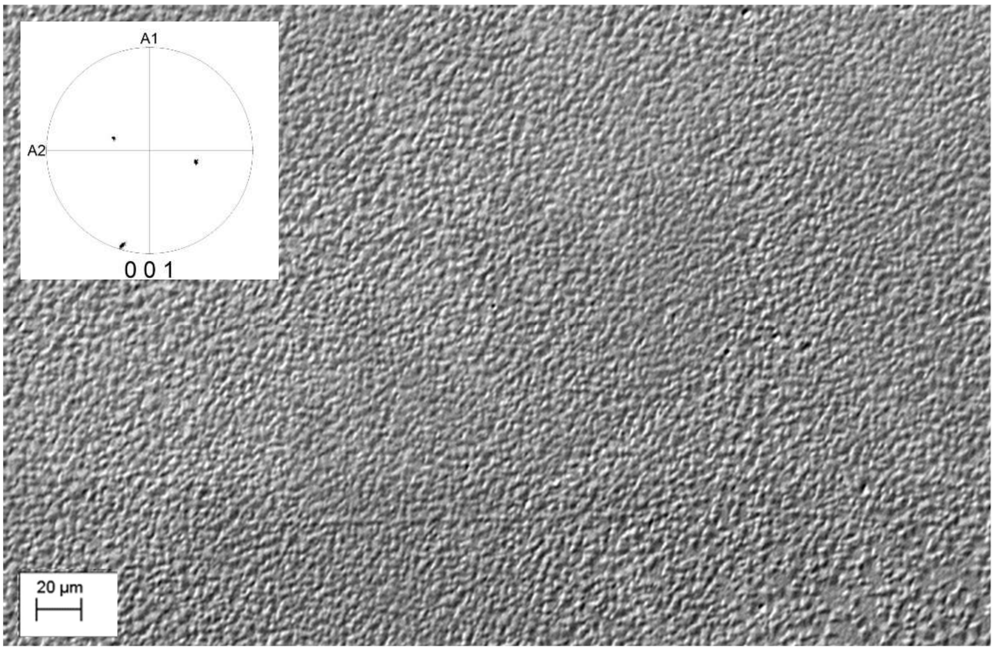


Figure 6 Secondary electron image of an undercooled Cu specimen (ΔT = 50 K) revealing dendritic structure and EBSD pole figure plot (insert); the 3 poles at 90º to each other confirm single crystal growth.

However, at high undercoolings ($\Delta T > 200$ K) a transition from a coarse grained to a grain refined structure was observed. This is evident from the Optical Micrograph and respective pole figure plot shown in **Figure 7**. From the dendritic substructure, revealed by the etchant, it is also evident that there are spherical elements within the individual grains, which can be suggestive of dendrite fragmentation. However, there are also a number of grains containing sub-grain boundaries, thus indicating that recrystallization could be the driving force for this transition. If recrystallization only was the cause of grain refinement, then a reduction in mechanical strength is to be expected. This has been confirmed in one of our earlier papers by microhardness measurements [12]. However, in this research this is not the case, as our results show that the mechanical properties increase with increase in the level of undercooling. Therefore, it may not be unreasonable to suggest that a combination of both mechanisms could have led to the formation of the refined structure at this level of undercooling, most likely to be in the order of initial dendrite fragmentation, taking place during solidification, followed by recrystallization, most probably induced by the residual heat within the undercooled copper specimen.

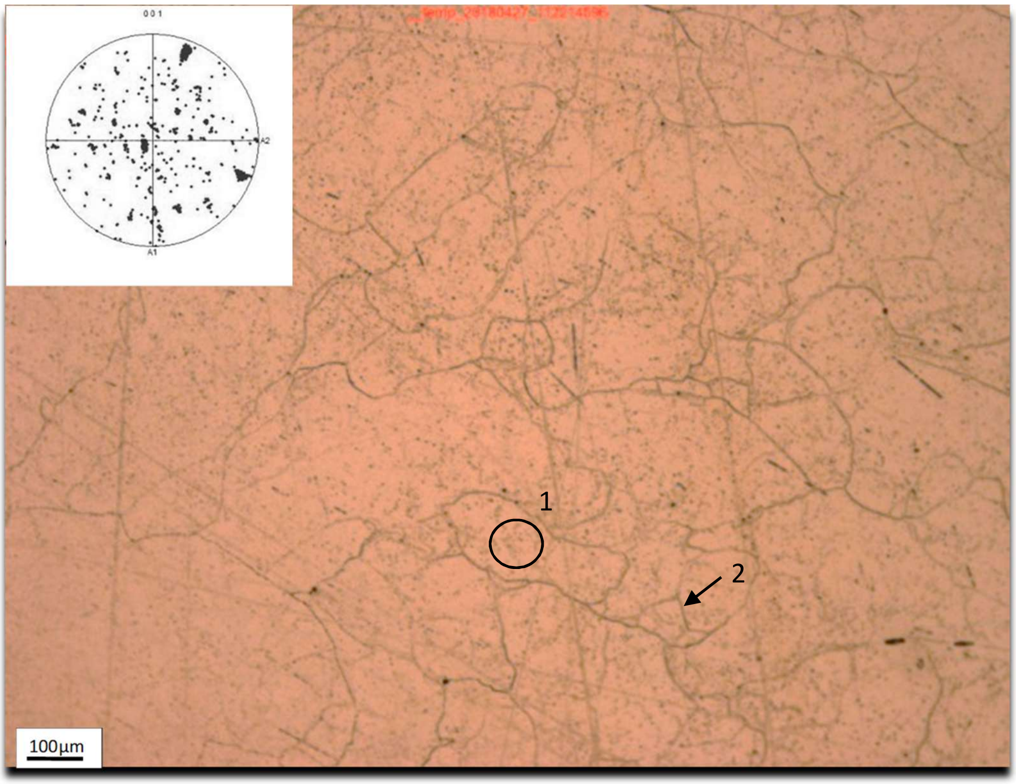


Figure 7 Optical micrograph (polarised light) and pole figure plot (insert) of a Cu specimen undercooled by 207K prior to nucleation. The large number of poles conclusively indicate that at this level of undercooling grain refinement has taken place; 1 – area showing spherical elements, which are the result of dendrite break up and 2 – example of sub-grain boundaries indicative of recrystallization.

Undercooled Cu modelling – Hall-Petch Law

In the final part of this study we adopt the Hall-Petch model to investigate the relationship between flow stress and grain size. It is obviously only possible to do that for the case of high undercoolings, as this is where polycrystal structures were observed in this study. For this, the etching method was used to determine the grain size of the undercooled specimens. Once it became apparent that those at high undercoolings formed fairly large grains, standard estimations of grain size, such as the Comparison Procedure and Planimetric Procedure were deemed not valid, as the grain boundaries were insufficient in number. Hence, the Intercept method was used to find the average number of grains across 4 intercept lines to produce an average grain size of 325 microns with standard deviation of 44 microns for an undercooling of 207 K [21]. This was compared to data obtained in our earlier studies [22] and it was confirmed that it is of the same order of magnitude. The predicted stresses for different strain rates were calculated using the following parameters: K = 5 [23], x = 0.5 (quasi static) and x = 1 (high strain rate) respectively [24], with σ_0, being the experimentally measured stress of what here is loosely defined as a 'single' crystal and in this case 137 MPa for quasi static and 216 MPa for high rate. The reason for making this assumption is that at these levels of undercooling solidification not always proceeds via single grain growth and on many occasions results in a coarse grained structure, usually 2, 3 very large grains [22]. However, the values used are similar to those reported in a previous study by Liu et al. [25] and therefore deemed suitable for the predictive calculation. From this, the predicted stress for quasistatic strain rate is 126MPa, which is approximately 8% lower than the experimental value and for high strain rate the calculated stress in 217MPa, or 1MPa (0.5%) higher than the measured one. From the data, also plotted in **Figure 8**, it is evident that for this particular dataset the experimental results fit well with the Hall-Petch law. However, this does not account for the observed break in the undercooling-stress relationship, which is clearly associated with a change in microstructure and therefore care needs to be taken when adopting this approach and a number of factors need to be considered: (1) when using this model obviously single grained specimens, obtained at various undercoolings, should not be included; (2) the methodology used for determining the actual grain size in specimens, with complex structures, e.g. where sub-grain boundaries are present could potentially affect the results; (3) for material systems which exhibit grain refinement at both low and high undercoolings, of for those where a break in the undercooling-property relationship is observed, the model is unlikely to be representative range and alternatives may have to be considered.

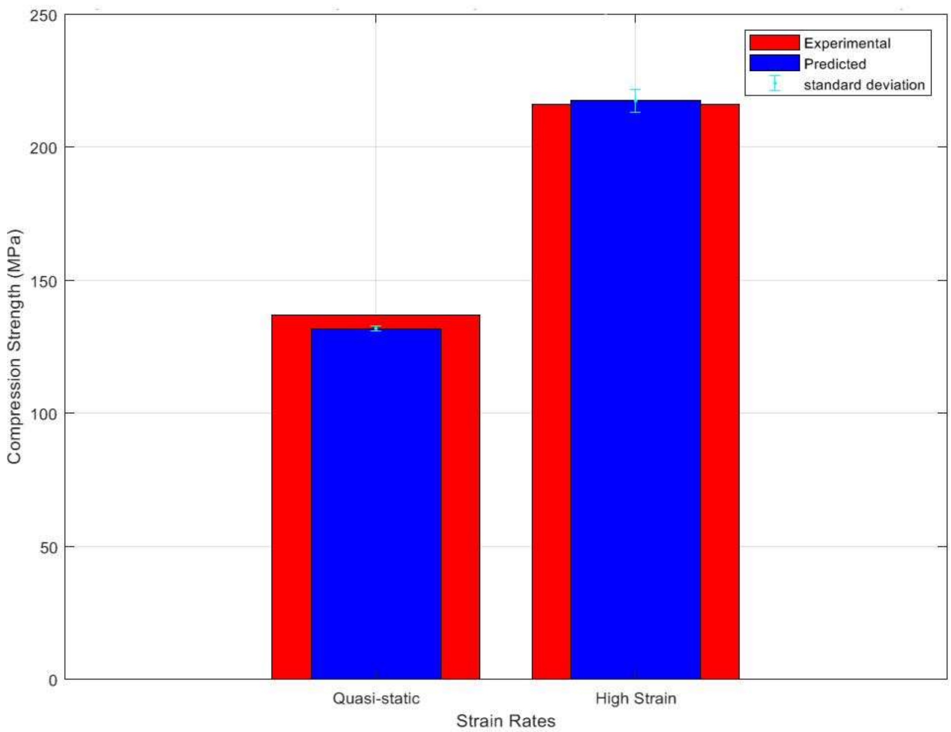


Figure 8 Comparison of predicted and experimental results based on the Hall-Petch law (Experimental values for polycrystal from high undercooling for Quasistatic and High strain rates on graph in red & in blue, the predicted values for a polycrystal, again high undercooling, for both Quasistatic and High rates of strain).

Conclusions

In this study, the mechanical properties of Cu specimens, obtained by means of high melt undercooling, were successfully investigated, for the first time ever, at two different rates of strain – quasistatic and high. It was found that irrespective of the strain rate, the specimens did not fail, but after yielding continued to deform until the test limit was reached. It was also found that under quasistatic conditions the specimens yielded at stresses in the region of 120 - 140MPa, whereas at high impact velocities the undercooled samples yielded at much higher stresses in the region of 215MPa. This therefore indicates that the flow stress in the studied undercooled material increases with increasing the strain rate. Further microstructural analysis revealed that at low undercoolings solidification occurred via coarse and/or single crystal growth, whereas high undercoolings resulted in the observation of grain refined microstructures. On this occasion, it is suggested that rather than a single mechanism, which is commonly proposed, a combination of dendrite fragmentation and recrystallization could be behind this transition. With regards to the increase in flow stress, at high undercoolings, this can be linked to the structural refinement observed and for low and moderate undercoolings the effects of non-equilibrium solidification should be taken into account. The significant increase in strength measured at high rates of strain can also be associated with an increase in dislocation density caused by the high impact velocities. Overall, it is strongly believed that the experimental results presented and discussed here, not only complement, but also enhance the current understanding of the complex processes during rapid solidification.

Conflict of Interest

The authors declare that they have no conflict of interest.

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