Abstract
This paper presents a microstructural study of laser micro-processed high purity Cu45Zr48Al7 alloys prepared by arc melting and Cu-mould casting. Micro-processing of the Cu45Zr48Al7 alloy was performed using a Rofin DC-015 diffusion-cooled CO\textsubscript{2} slab laser system with 10.6 µm wavelength. The laser was defocused to a spot size of 0.2 mm on the sample surface. The laser parameters were set to give 300 and 350 W peak power, 30% duty cycle and a 3000 Hz laser pulse repetition frequency (PRF). The PRF and duty cycle resulted a 0.1 ms pulse duration. About 100 micrometer wide channels were scribed on the surfaces of disk shaped amorphous and partially crystalline samples at traverse speeds of 500 and 5000 mm/min. These channels were analysed using scanning electron microscopy (SEM) and 2D stylus profilometry. The metallographic study and profile of these processed regions are discussed in terms of the applied laser processing parameters. The SEM micrographs showed that striation marks developed at the edge and inside these regions as a result of the laser processing. Grain formation occurred with the processed regions for processing traverse speeds of 500 mm/min in the partially crystalline samples. For the amorphous structure, channel widths of 149.6 µm, 102.2 µm and 77.4 µm were measured. Using the same processing parameters, channel widths of 158.4 µm, 122.0 µm and 91.2 µm were measured on the partially crystalline alloy surface. The scribed regions showed a maximum depth of 1.4 µm and interesting height increases above the original sample surface height of 2 µm on the amorphous sample. Micro-segregation was recorded on the samples surfaces at processing parameters of 300 W and 7.20 ms exposure time in both the amorphous and crystalline samples. The results from this work showed that micro-scale features can be produced on the surface of amorphous Cu-Zr-Al alloys by CO\textsubscript{2} laser processing.

PACS 87.85.Va · 64.70.pe · 68.37.Hk

1.0 Introduction
In many applications, amorphous metallic alloy or bulk metallic glass (BMG) is potential for replacement of conventional engineering materials like metals and polymers. The BMG materials exhibited better mechanical and physical properties compared to the other crystalline metallic alloys. Additionally, the metallic glasses are more resistant to fracture than covalent glasses or ceramics. It has high hardness and also provides a combination of metallic high strength with elasticity as high as that of polymers [1].

Casting is the most typical method in mass production of BMG which capable of resulting in acceptable dimension accuracy. However, secondary process like machining is vital to deal with stringent dimensional accuracy and surface roughness requirements [2]. In conventional turning and drilling processes, low thermal conductivity of BMG leads to high temperatures generation during chips machining [2]. While producing amorphous alloy materials is challenging, the conventional contact machining has drawback with the cutting tools coating suitability on BMG materials [2]. Recent works on non contact micro-machining of BMG was later done using micro-electro-discharge machining (MEDM) to produce micro-holes [3]. In micro-machining of BMG, the heat generated is difficult to diffuse into the base material, which causes large heat affected zone [3].

It is difficult to manufacture micro or nano-size features in crystalline metallic structures, due to the presence of grains. BMG is homogeneous and applicable for nano-scale geometries [4]. Therefore, amorphous metallic structures are becoming more popular for this purpose. Recent attempts of BMG application in micro-scale are precision spur gear, wheel like micro-components, and moulds for aspheric lens fabrication [5-7]. Although, there are huge potential of manufacturing micro and nano-size features in BMGs, there are only a few application currently focusing on this area. This work is significant to expand the
knowledge on processing micro-features and micro-channels on amorphous alloys. In this paper the effects of laser parameter settings on amorphous and partially crystalline Cu-Zr-Al alloy microstructures were investigated.

2.0 Experimental

Bulk metallic glass rods of Cu45Zr48Al7 composition were produced by arc melting the high purity components and Cu mould casting the ingot from liquid state. Samples of 5 mm diameter and 4 mm thickness were cut from the as-cast rods and were processed and examined in this study. X-ray diffraction patterns of the samples were recorded using a Bruker D8 XRD system with Cu Ka ($\lambda = 1.5405$ Å) radiation. The diffraction patterns were recorded in the 2$\theta$ range of 20 to 80˚. Samples were mounted in Bakelite and polished before processing to allow clear difference in surface microstructure to be identified. The flat 5 mm diameter surfaces were laser processed by a single pass of the sample across its diameter beneath the pulsing laser beam. The sample surface was held perpendicular to the laser beam firing direction during this translation. A CO2 laser with a defocused circular spot diameter of 0.2 mm on the sample surface was used. The beam quality was TEMoo. The PRF and duty cycle were constant at 3000 Hz and 30% respectively for all experiments. The scribed line (micro-channel 1) was processed at 300 W laser power and 500 mm/min to achieve 0.03 J pulse energy and exposure time of 7.20 ms respectively. For the second case (micro-channel 2), the laser power was set at 350 W to provide 0.035 J pulse energy and traverse speed was set at 5000 mm/min. For the third case (micro-channel 3) was processed at 300 W laser power and 5000 mm/min. From the 5000 mm/min traverse speed, a shorter exposure time of 0.72 ms was achieved. These parameter settings were chosen to produce rapid melting along lines (micro-channels) with of about 100 micrometer width. Flowing argon gas was applied during processing at a pressure of one bar. The depths for all micro-channels were measured using a 2D TR200 stylus profilometer integrated with TimeSurf software for data acquisition. The processed surface was examined with an EVO-LS15 Scanning Electron Microscope (SEM).

3.0 Results and Discussion

Figure 1 shows the XRD pattern of two as-cast sample disks. The broad maxima in Figure 1(a) indicate the existence of amorphous phase in the cast sample. The partially crystalline pattern in Figure 1(b) shows, the broad maxima were also detected along with CuZr and ZrO$_2$ crystalline peaks. Figure 2 shows the SEM micrographs of micro-channels machined on the sample surface at the three different laser parameter settings for both the fully amorphous and the partially crystalline samples. The average width of micro-channels 1 on the amorphous alloy was 150 µm as shown in Figure 2(a). The widths of the micro-channels 2 and 3 on the amorphous alloy were measured as 102 µm and 78 µm respectively (see Figure 2(b) and (c)). At the higher exposure time for micro-channel 1, a wider heat affected region and corresponding channel width resulted compared to micro-channel 2 and 3. This was due to higher temperature generated on the surface at the higher exposure time. For a similar reason, the higher power for line 2 produced a wider line compared to line 3. In partially crystalline alloy, the widths of lines 1, 2 and 3 were measured as 158 µm, 122 µm and 91 µm respectively as shown in Figure 2(d), (e) and (f).

The edge of the heat affected line region is clearly visible in the micrographs. Both
amorphous and partially crystalline samples exhibited striation marks at the edges and inside the micro-channel. Coarse striation marks perpendicular to the micro-channels were visible at the edges while fine striation marks found inside the channels pointing in the direction of processing. More striation marks were observed in micro-channel 1 compared to the other two channels. Interestingly, a strong contrast indicating the presence of micro-grains was also found in the partially crystalline sample (in micro-channel 1). Figure 3(a) shows a higher magnification SEM micrograph of the structure shown in Figure 2(d). Grains within a size range of 1 to 3 µm were developed between the striation marks. Similar grains were not found in the other two channels; see Figure 3(b) for comparison which represents a high magnification micrograph of Figure 2(f).

The surface troughs measured in both amorphous and partially crystalline alloy were between 0.8 to 1.4 µm deep. Figure 4 shows the 2D profile measured across micro-channels of the amorphous Cu-Zr-Al alloy sample. The maximum depth of the channel measured was approximately 1.4 µm. Increase of material volume was observed in the middle of the channel due to either volume conservation or phase change during laser processing.

The amount of energy provided was sufficient to melt a definite volume of material on the BMG surface. BMG samples typically exhibit lower thermal conductivity relative to their crystalline counterpart [9]. The thermal conductivity should affect the micro-feature formation. This could explain the larger micro-line widths measured in the partially crystalline alloy due to its higher thermal conductivity compared to the amorphous material. Lower thermal conductivity material would reduce the
heat flux to the surrounding area and into the surface. Less difference was noticed with respect to feature depth and height between these materials. Striation mark formation at the channel edges was most likely due to thermal strains occurring in the material during rapid cooling from the millisecond exposure time frames. The large energy density from micro-channel 1 processing conditions would have caused slower cooling rates within the channel surface. The exposure time for channel 1 was 7.20 ms which is ten times higher than for channel 2 and 3 processing conditions.

![Figure 3: Striation marks for partially crystalline Cu-Zr-Al alloy in (a) line 1 with evidence of micro-grain formation and (b) line 2 without evidence of micro-grains.](image)

![Figure 4: 2D profile across line 2 of amorphous Cu-Zr-Al alloy.](image)

### 4.0 Conclusion
The results from this work showed that micro-scale channel and features can be produced on the surface of amorphous Cu-Zr-Al alloy. A range of channel depths from 0.8 to 1.4 µm were measured in the amorphous and partially crystalline Cu-Zr-Al alloy. The channel widths measured in the amorphous sample were lower than in the partially crystalline channels most likely due to its low thermal conductivity. The laser machining parameters for creating micro-channels on amorphous Cu-Zr-Al alloy samples can be controlled to avoid recrystallisation. By using 300 W of laser power and 7.20 ms exposure time, the cooling rate was slow enough to form micro-grains from the pre-existing nuclei in channel 1. No micro-grains were observed for lines 2 and 3, where the power was set at 300 and 350 W and exposure time was kept at 0.72 ms. Striations were found to varying degrees in all scribed micro-channels. This could allow for the possibility of increasing wear resistance in industrial engineering components or directing fluid flow in micro-moulding.

### Acknowledgements
The authors are grateful to Enterprise Ireland for providing Commercialisation Fund, Technology Development support to enable manufacture of the BMG rod samples.

### 5.0 References