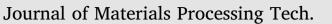
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## Laser processing of bulk metallic glass: A review

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### ABSTRACT

The emergence of bulk metallic glasses and their identification as versatile advanced engineering materials with attractive properties has led to a surge in research efforts to investigate processing methods, which can be used either to synthesise new BMG alloys or to shape BMG workpieces into final components with specific geometries. Among such technologies, the number of studies focussing on the laser processing of BMGs has gradually increased over the past decade. For this reason, a comprehensive summary of the state-of-the-art in this particular field of research is presented in this review. The reported studies are categorised into the different laser applications that have been proposed so far by the research community, namely the welding, cladding, additive layer manufacturing, micro machining and microstructure modification of BMG substrates. Due to the attractive properties of BMGs stemming from their amorphous nature, results are also presented, when available, concerning the effect of laser irradiation on the generation of crystalline precipitates during processing and the effect of these changes on the resulting material properties. This review has identified a number of gaps in the knowledge surrounding the laser processing of bulk metallic glasses. Understanding the fundamental interaction of laser energy with multi-component alloys will be necessary, as the development of lasers continues and the amount of available bulk metallic glasses increases. In particular, the crystallisation kinetics of bulk metallic glasses during laser irradiation needs to be understood to aid in the development and optimisation of processes such as welding and cladding. This could be helped by created an accurate simulation model to predict the onset of crystallisation although this is not a minor challenge, developing a complete temperature field model during laser irradiation is a complex task when considering vaporisation, plasma effects as well as chemical composition changes in the material. Besides, there is also the issue of variations in material properties as the temperature increases, particularly for BMGs whose temperature dependent properties are not well-documented. The research into the additive layer manufacturing of bulk metallic glass should continue to grow. Parametric effects need to be addressed to complete the optimisation of this process. Further investigations of the resulting crystallisation processes upon repeated melting and solidification should also aid in the process being able to be controlled more effectively. Finally, the use of laser processing of bulk metallic glass for specific application needs to be investigated further.

#### 1. Introduction

Bulk metallic glasses are an emerging family of advanced engineering materials that have inherent attractive properties, ranging from their superior hardness, good corrosion resistance to a large elastic strain limit (Peker and Johnson, 1993). In the last decade, a number of reviews have been published related to the synthesis, properties and applications of this class of materials. The review by Axinte (2012) discussed the history of bulk metallic glasses, their properties and their applications. The author concluded that the future for these materials was destined to be bright with advances in thermoplastic forming and specially designed structural bulk metallic glasses predicted. Schroers (2010) presented a detailed review of the processing of bulk metallic glasses, including the casting and thermoplastic forming and their effect on the material properties. Lu and Liu (2004) reviewed the role of minor alloying additions during the formation of bulk metallic glasses, presenting the effect on various types of alloying on the material properties. In order to complement the information reported in these reviews, the specific aim of this paper is to present the current state-of-the-art in the processing of bulk metallic glasses using laser given that this is a field of research which has gained increased interest in the last decade.

In 1960 the first metallic glass was reported by a group at California Institute of Technology (Klement et al., 1960) and their development

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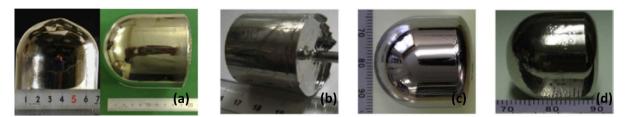


Fig. 1.1. Different types of bulk metallic glass ingots (a) Pd-Cu-Ni-P, (b) Zr-Al-Ni-Cu, (c) Cu-Zr-Al-Ag and (d) Ni-Pd-P-B (Inoue and Takeuchi, 2011).

was continued by Chen et al. during the 1970s. This new material had the internal amorphous structure of a glass whilst its constituent parts were metallic elements. In order to develop these materials, the liquid phase of the metallic elements is cooled as quickly as possible, quicker than a specific critical cooling rate. Cooling quicker than this rate results in free atoms not having enough time to organise themselves into an ordered metallic lattice. Needing a very high cooling rate to create these disordered lattice restricted early fabrication attempts to very thin dimensions to allow fast heat dissipation.

Today, a number of different amorphous metallic alloys can be produced with dimensions in the range of a few centimetres such as those reported by Inoue and Takeuchi (2011) in Fig. 1.1.

Table1.1 displays a comparison between the properties of metals, glasses and metallic glasses.

These properties make bulk metallic glasses ideal candidate for many different applications across many industrial sectors, as reported by Inoue and Takeuchi (2011).

The amorphous structure of a material with the properties of metal results in the unique ability to form bulk metallic glasses like plastic. Schroers et al. (2007) were able to process BMG with thermoplastic forming for MEMS fabrication by raising the temperature of the material in the super cooled liquid region for a duration short enough to avoid the onset of crystallisation. They concluded that being able to replicate 100 nm features in a similar way to plastic but with a material that has a high-strength, produces a wide range of applications for microstructures and MEMS fabrication. This ability to be formed like plastic also provides interesting prospect to the biomedical industry, as BMGs exhibit a strength and elasticity that exceeds most biomaterials. In particular, Schroers et al. (2009) conducted biocompatibility tests and concluded that a number of BMGs could be used successfully as biomedical implants.

The versatility of laser processing and the desirable properties of bulk metallic glasses have resulted in a variety of publications focusing on laser welding, cladding and coating and the more recent development of additive layer manufacturing of bulk metallic glass structures. The use of lasers to process bulk metallic glass will ultimately produce heating and cooling cycles within the material. Due to the properties of BMGs being directly linked with their amorphous structure, it is desirable for these heating and cooling cycles to be within a range whereby they do not induce crystallisation precipitates into the microstructure of the material. Glass forming ability (GFA) charac-

 Table 1.1

 Comparison of the properties of metals, glasses and metallic glasses.

 Adapted from Anantharaman (1984).

Property	Metal	Glass	Metallic glass
Structure	Crystalline	Amorphous	Amorphous
Interatomic bonding	Metallic	Covalent	Metallic
Yield stress	Non-ideal	Almost-ideal	Almost-ideal
Hardness	Various	Very high	Very high
Optical nature	Opaque	Transparent	Opaque
Conductivity	Good	Poor	Very good
Resistance	Low	High	Very low
Corrosion resistance	Various	Very good	Very good
Magnetic properties	Various	None	Various

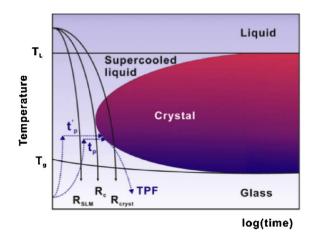


Fig. 1.2. A schematic diagram of the continuous cooling curve for bulk metallic glasses (Pauly et al., 2013).

terises the ability of a BMG to withstand crystallisation. Greer (2015) states that this property will scale inversely with the cooling rate induced in a BMG. This means that a higher cooling rate necessary to avoid crystallisation within a particular BMG, the lower its GFA. With respect to laser processing, if the material has a low GFA then the cooling rate necessary to keep its amorphous structure will be high, possibly too high for the cycles induced during processing. Fig. 1.2 from the work of Pauly et al. (2013) describes the continuous-cooling (CC) diagram for the specific BMG studied. If the cooling curves induced during laser processing intercept with the CC curves for the BMG then crystallisation may occur.

In this context this review aims to present recent research on the laser processing of bulk metallic glass, in particular laser welding, cladding, additive layer manufacturing, micro machining, and the use of laser processing to deliberately alter the properties of the BMG material. The review will focus on laser processing of bulk metallic glasses although laser processing of thin metallic glass samples has also been conducted. In particular, Zheng et al. (2013) studied the dynamic fracture behaviour of Fe-based metallic glass having used lasers to produce a shock load and Otsu et al. (2009) utilised YAG lasers to bend a thin sample of palladium based metallic glass without crystallisation. Finally, concluding remarks concerning the future of laser processing of bulk metallic glasses are provided in the last section.

#### 2. Laser welding of bulk metallic glasses

#### 2.1. Introduction to laser welding

Laser welding utilises high energy laser beams, scanned across the surface of two adjacent materials, to create a small diameter keyhole where the material has been vaporised. Within this keyhole, the vapour pressure prevents the molten wall, created when the laser beam scans the material, from collapsing. As this keyhole is moved along the surface it leaves a trail of molten material which forms the seal between the two joined materials. Fig. 2.1 shows a schematic of how laser keyhole welding operates in practice (Dawes, 1992).

For bulk metallic glasses, laser welding is particularly useful. This is

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