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WEDM-LS processing sophisticated and durable Zr-based metallic glass mold insert for micro structure injection of polymers

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Abstract
Micro components processed by injection molding still have a defect of bad precision and short life. A Zr- based metallic glass was reported for injection mold insert which can solve the problem well. The microstructure of metallic glass mold insert can be fabricated by wire electrical discharge machining-low speed (WEDM-LS), WEDM-LS has higher machining accuracy than WEDM-high speed, and X-ray diffraction curves show that the processed sample still retained better amorphous characteristic, afterward, time-temperature-transformation diagram shows metallic glass has a long service life in production. Finally, under the observe of scanning electron microscope, it is found that the products after injection molding not only completely replicates the structure on metallic glass but also have a better surface morphology. These experiments show that processing a sophisticated and durable Zr-based metallic glass mold by WEDM-LS is good for getting micro structure injection of polymers. It also provides a good mold material and machining method for injection industry.

Keywords Metallic glass · Microstructure · Wire electrical discharge machining-low speed · X-ray diffraction · Time-temperature-transformation

1 Introduction

The development of micro-electro-mechanical systems (MEMS) and micro-systems requires reliable large-scale manufacturing processes to fabricate micro-components with micron/nano-scale characteristics (Zhang et al. 2012a, b). Although the micro-structure technology of metal devices is relatively mature, there are still shortcomings of time-consuming and high cost. Compared with metal devices, plastic devices not only have the advantages of lighter weight which the quality of a plastic device is about 1/6 of the same volume of metal but also easier to produce (usually less than10s to form a product). Therefore, plastic micro devices have ushered in a spring, they are widely used in MEMS and have been widely studied and applied in biology, physics, optics and so on (Heckele and Schomburg 2004; Mitcheson et al. 2004; Yi et al. 2008). At present, most of micro plastic devices are manufactured by injection molding, however, there is still a problem about the accuracy and life of mold used for producing micro injection devices, at the same time, it also puts forward higher requirements for mechanical properties of materials and more efficient processing technology.

Because bulk metallic glasses (BMGs) exhibits superior mechanical properties like high yield strength, elasticity, hardness and fracture toughness, high wear and corrosion resistance (Argon 1979; Inoue 2000; Ashby and Greer 2006; Lewandowski and Greer 2006; Eckert et al. 2007; Chen 2008; Wang 2012), making it an ideal material for microstructures injection molding. To explore a suitable BMG for micro injection molding process, many researchers have studied it from the aspects of preparation, material, forming technology and so on (Guo et al. 2009; Wang et al. 2009; Liu et al. 2011; Ma et al. 2012; Hu and Yan 2016). Compared to conventional machining methods, single point diamond turning, die-casting and hot embossing methods of BMGs in the supercooled liquid region (Saotome et al. 2001; Schroers 2005; Wiest et al. 2009; Johnson et al. 2011), all have successfully fabricated micro/nano-scale structures such as micro-gear, microchannel, superhydrophobic structure and so on. Zhang, N et al. (Zhang

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et al. 2012a, b) reported that the service life of Zr-based BMG as a mold insert can reach 20,000 cycles without affecting the precision of plastic parts. These shows that the inset using metallic glass as injection mold has predictable great future in injection direction. However, when using these methods to form microstructures, there are some shortcomings such as high processing cost, limited processing size, and because the materials are exposed to air, the oxidation and crystallization of BMG is easy to occur with the increase of processing temperature. Therefore, a new process of lower cost and more efficiency has been proposed to produce microstructures and avoid oxidation in BMG mold inset.

Wire electrical discharge machining-low speed (WEDM-LS) as a new process for machining Zr-based BMG microstructures. It is a process of heating, melting and curing metallic glass by discharge (Mingqi et al. 2005; Hu and Yan 2015). If unsuitable heating and cooling processes are experienced by the part, crystallization will be inevitable, which lowers surface accuracy, mechanical and chemical property advantages of BMGs (Yeo et al. 2009; Garg et al. 2010; Gu et al. 2010). Because the WEDM-LS processing material is completely immersed in the oil environment during processing, the effect of external oxygen on the surface of the material is well prevented. At the same time, the oil environment takes away the heat accumulated on the surface of the material during processing, thus avoiding the crystallization of BMG due to the excessive surface temperature during continuous processing. In WEDM-LS process, thin metal wires moving continuously in one direction and at low speed are used as electrodes to remove materials by intermittent pulse discharge. The microstructure of BMG is fabricated in the machining of line electrode movement. Even if the loss of fine wire occurs during processing, it can be continuously supplemented, thus improving the manufacturing accuracy. Its general traveling speed is less than 0.2 mm/s and the accuracy can achieve 0.001 mm (Kunieda and Furudate 2001; Mahapatra and Patnaik 2007; Garg et al. 2010; Gong et al. 2016). The electrode wire is no longer used after discharge. Its maximum productivity can reach 350 mm^2/min which greatly improves the efficiency of the production of molds. Up to now, using WEDM-LS to processing Zr-based BMG microstructure has not been reported yet, in this study, the surface structure of BMG after WEDM-LS machining and injection molding parts were observed. After that, we debated the carbonization and crystallization of the machined surfaces of the BMG. Finally, the mechanical properties and service life of Zr-based mold inset were analyzed.

2 Experimental

$Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ (at. %) BMG was used for this experiment. First, the arc discharge copper mold suction casting method was used to get an amorphous cylindrical rod with diameter of 7 mm, and cut it into 3 mm thickness using a low-speed diamond cutting machine. Then polish its surface with 400, 800, 1200, 1500, 2000 sandpaper and polishing machine. The amorphous nature of the Zr-based metallic glasses were ascertained by x-ray diffraction (XRD, Rigaku-miniflex600, Japan) with Cu K_α radiation and differential scanning calorimetry (DSC; PerkinElmer-DSC8000, American) at a heating rate of 20 K/min. After that, the WEDM-LS (Sodick-LPW250, Japan) was chosen for forming its micro-structures, in this process, a row of μm 130 μm wide grooves were fabricated, again, XRD was used to characterize the amorphous properties of sample. Next, a structure from the center part of the injection mold was removed, and use the sample to embedding it, complete the assembly of the mold, and put it into the world's smallest injection molding machine (Babyplast-6/10P, Italy) to produce plastic products, its minimum injection product quality is 10 mg. the whole injection design process is presented in Fig. 1.

Polypropylene (PP) and Polyethylene (PE) materials were used in the injection experiment, the experimental parameters are shown in Table 1, the data in the table are obtained from repeated experiments with experimental equipment. After getting the products, the surface of PP, PE and Zr-based BMG were obtained by a scanning electron microscope (SEM; Hitachi-SU70, Japan).

3 Results and discussions

Figure 2a shows the processing schematic of WEDM-LS and Fig. 2b is an enlarged surface sketch of the red dotted boxes in Fig. 2a. $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ metallic glass sample completely immersed in the oil environment, it acts as a barrier to oxygen and takes away heat from the machined surface. The sample surface structure processing by Cu electrode wire pulse discharge. The SV voltage between the electrode wire and the workpiece is set to 120, and the capacitance is in mode 1, 130 μm diameter copper wire is used as wire electrode cutting material, pulse current turns on 60 ms and off 40 ms in a cycle. Here, we assume a curve in Fig. 2c that the surface temperature of a sample varies with time, and the temperature is always below the crystallization temperature. It matches the pulse period and shows periodic rise and fall.

The WEDM-LS processed Zr-based BMG is assembled and as mold to produce plastic products as shown in Fig. 1. The surface morphologies of PE, PP plastic parts and mold were obtained by SEM. Figure 3a is the BMG surface morphologies, the width of the groove is 130 μm, the width of the ridge is 140 μm. Figure 3b, c show PE, PP plastic products replicate the microstructure of the MG mold inset very well and the surface roughness of plastic parts is much smaller than that of mold. Image demonstrated that the polymer products manufactured with BMG insert have an error less than 10 μm.

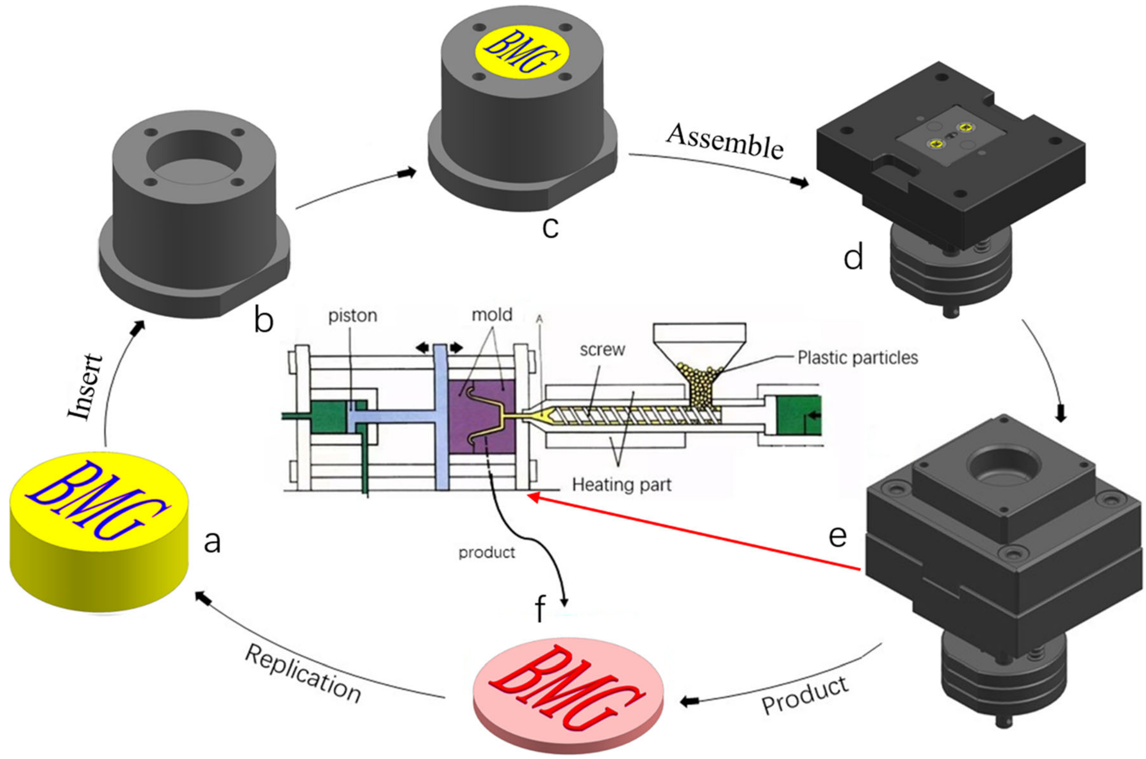

Fig. 1 From a to f show the flow chart of the whole set of injection molds design and production process of Babyplast injection molding machine. a is the Zr-based BMG mold insert and f is the injection molded products

This is mainly due to the shrinkage of polymers cooling. However, it is inevitable in the process of injection molding. The formula for calculating the shrinkage rate can be described as in Eq. 1:

$$S = \frac{L_c - L_s}{L_c} \times 100\% \tag{1}$$

Where L_c is the unidirectional dimension of the polymers at the injecting temperature, L_s is Unidirectional dimensions of polymers at room temperature. According to Eq. 1, the calculated S value for PE, PP are 6.8%, 2% respectively. The smaller the value, the higher the accuracy of the replication. The improvement of surface roughness and replication accuracy will be further studied by controlling processing parameters in future research.

$Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ (at. %) rod with a diameter of 7 mm was obtained by means of arc discharge and copper mold suction casting. However, it is still unknown whether the $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ rod is amorphous nature. The XRD and DSC devices are important means to analyze it, as the Fig. 4a show, there is a dispersive diffraction peak on the curve indicates that we succeeded in getting an amorphous alloy. There are four sharp peaks at ~33°, 39°, 56°, 67° in the XRD curve of EDMed sample, by comparing the PDF cards, it is known that the four peaks are ZrC phase, the main reason is that the nano-carbide ZrC formed by the combination of oil-decomposed carbon and Zr element during discharge leads to the crystallization peak on the machined surface (Hu and Yan 2015).

The general trend of the curve still shows a diffuse peak indicate the mold surface still retained better amorphous characteristic. Figure 4b is the DSC curve of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$, as arrow indicates it exhibits a lager supercooled liquid region (SCLR), Its temperature range is calculated as follows Eq. 2:

$$\Delta T = T_x - T_g \tag{2}$$

where T_x is the onset temperature of the first crystallization event, T_g is glassy transition temperature, their values in Fig. 4b are 578 K, 737 K, respectively. The downward peak demonstrates the transformation of crystalline state during heating, further verifies that the obtained sample in Fig. 3a is

Table 1 Injection parameters for different polymers

Plastic code	Full name	Injection temperature [K]	Injection Pressure [MPa]	Hold time [s]
PE	Polyethylene	440~480	5	5
PP	Polypropylene	430~480	7	5

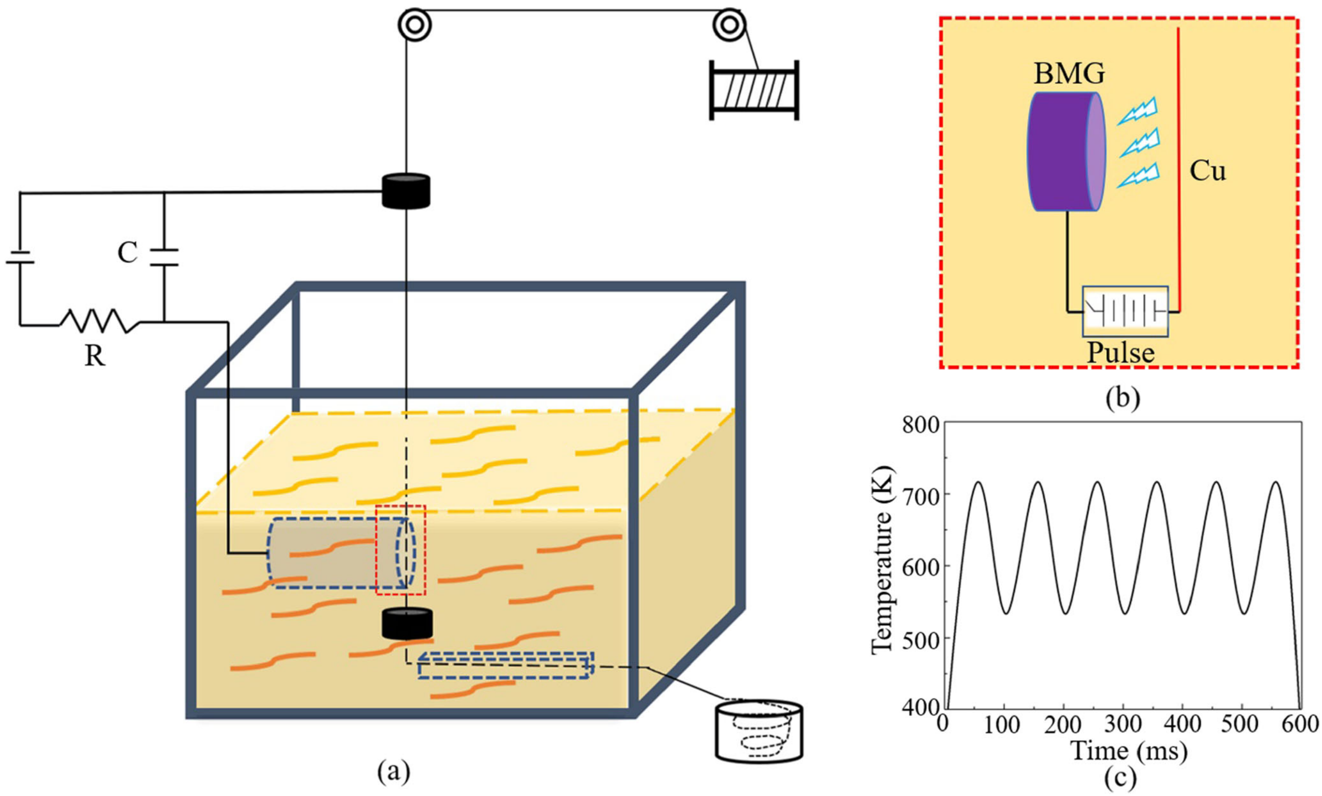

Fig. 2 **a** the processing schematic diagram of WEDM-LS **b** Copper wire is used as electrodes to process the micro-structure of dies by pulse discharge **c** a hypothetical curve of BMG surface temperature during pulse discharge

amorphous. Furthermore, the rationality of the hypothetical curve in Fig. 2c is also verified.

In Fig. 5, the mechanical properties of materials are usually considered. The fracture toughness of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ was estimated to be 85 MPa.m$^{1/2}$ and the yield strength of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ under uniaxial compressive texts was found to be 1.43 GPa, is better than PTFE (as a few times injection mold, the precision is not high, but the use of 3D printing is low cost) and Ni alloys (which is well known that there is a high yield strength 920 MPa and fracture toughness

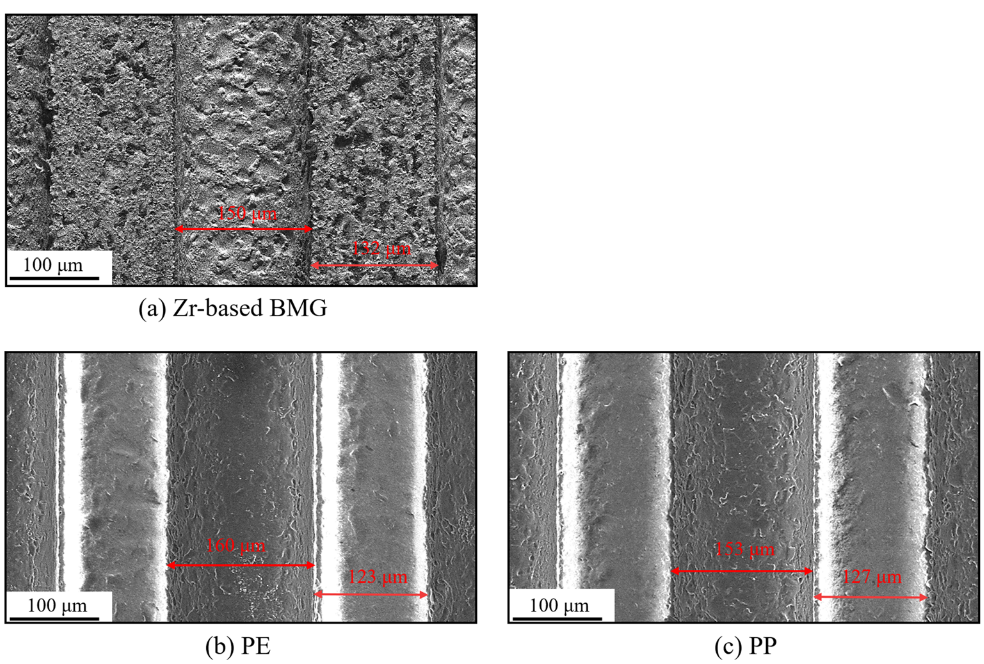

Fig. 3 Surface morphology of samples: **a** Zr-based BMG mold inset **b** PE **c** PP

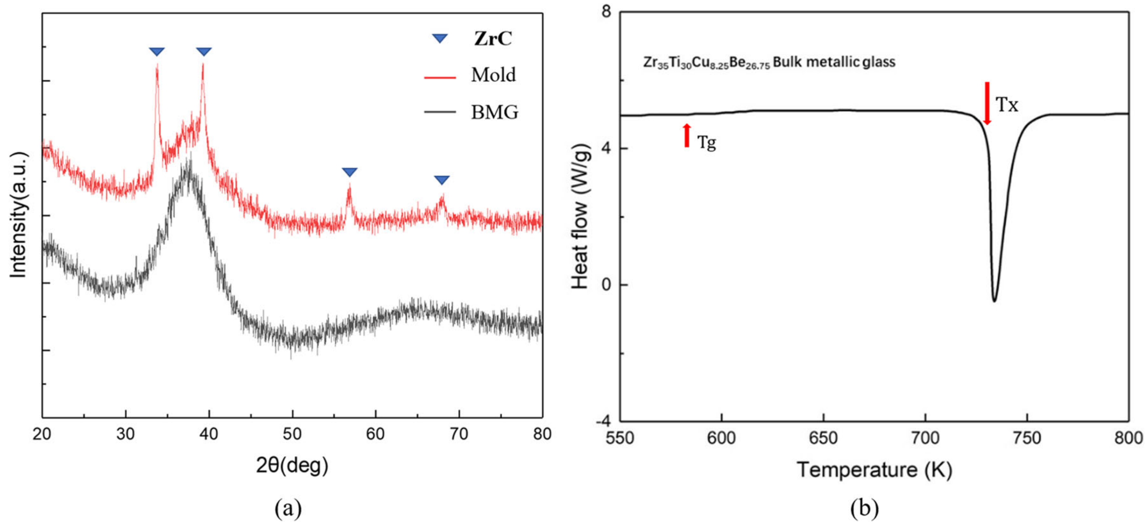

Fig. 4 **a** XRD patterns of the mold surface and unmachined surface of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ **b** DSC curve of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ metallic glass

117 $MPa.m^{1/2}$) (Avella et al. 2004; Yeh et al. 2004; Chiarbonello et al. 2006; Georgatis et al. 2013). Because of the BMG's superiority of mechanical properties, the replacement of stainless steel as the inset of the injection mold is just around the corner.

Crystallization is a clear shortage of BMG, this is due to its formation mechanism and dynamics problems caused the metallic glass to be a metastable state. The crystallization of metallic glasses is an inevitable trend, it will decrease the mechanical properties of the material and the surface quality become worse and worse, so that the BMG mold insert will no longer meet the requirements of the injection molding process, fortunately, this relaxation takes hundreds of years. On the other hand, higher temperature will accelerate its transformation to crystal, a temperature-time-transformation (TTT) curve was used to analyze this transformation. To avoid such crystallization process of materials, the temperature which is needed for the injection of polymers should to be considered. The same lucky thing is, for most plastic material such as Polyethylene (PE), Polypropylene (PP), Polyoxymethylene (POM), Acrylonitrile-butadiene styrene plastic (ABS), this temperature is below 520 K as shown in Table 1, which is far less than the crystallization temperature 737 K of the $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ MG. The temperature and time dependent transformation from amorphous to crystalline state of this MG can be summarized in a TTT diagram which was performed by isothermal crystallization studies, as presented in Fig. 6. Data points are collected from references (Duan et al. 2010), we extend the data to 400 K by curve fitting. On this curve, we can easily estimate the crystallization time of

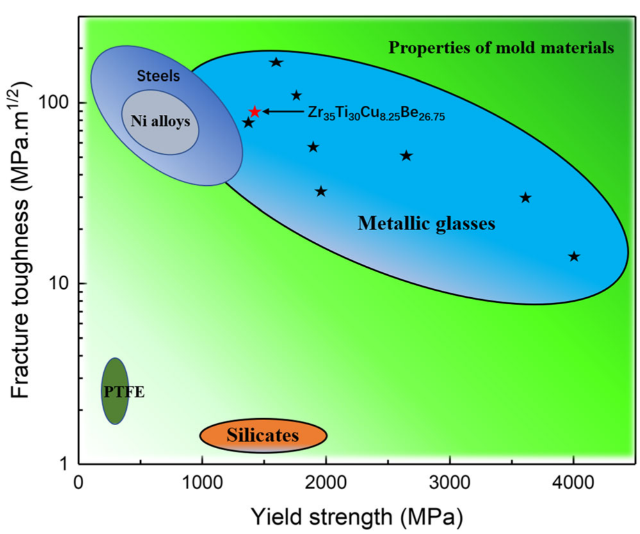

Fig. 5 The yield strength versus fracture toughness of some commonly used materials for injection mold inset. Including Silicates, PTFE, Ni alloys, Steels and metallic glasses, among them, the Red Pentagram pattern is the material of this experiment

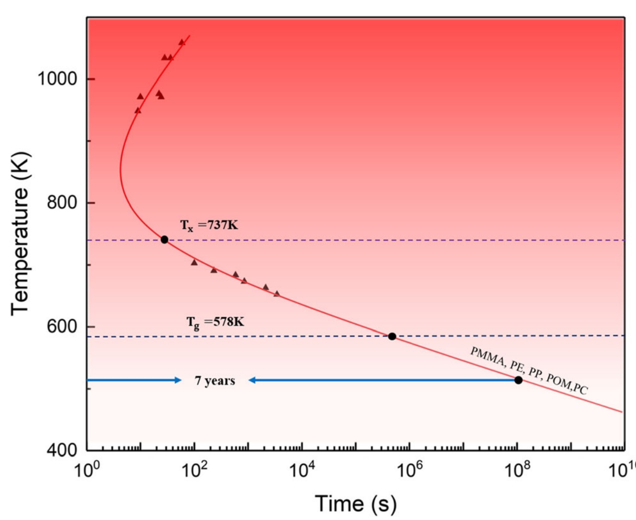

Fig. 6 Temperature-time-transformation (TTT) diagram of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ MG, extend the data to 400 K by curve fitting. Common injection molding temperature, such as PP, PC, PE, PMMA, POM, less than 520 K

$Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ MG at certain temperature. At the temperature of 520 K, it can be estimated that the working time of MG mold insert is 7 years. Considering the actual usage, the mold inset life will be longer that fully meet production requirements. All these discussions illustrate that the use of WEDM-LS as a new processing method to processing sophisticated and durable Zr-based metallic glass mold inset for micro structure injection of polymers is worthy of application and promotion.

4 Conclusions

In this study, the BMG microstructure was successfully fabricated by using WEDM-LS, and the XRD curve shows the samples did not crystallize, moreover, it can finish the micro-structure of the sample in a very short time with low cost. Using it to make the mold insert of injection, the injection product can reproduce the structure of the Zr-based BMG insert very well even has better surface topography, even with a 10 μm error. Although ZrC phase exists on the machined surface, it does not affect the mechanical properties and replication ability of amorphous materials. The mechanical properties image of BMGs materials shows excellent yield strength 1.43 GPa and fracture toughness 85 $MPa.m^{1/2}$. The analysis of the TTT proves that the BMG mold insert will serve more than 7 years under normal injection conditions. These experiments prove that using WEDM-LS to process BMG injection mold is hopeful to promote the development of MEMS.

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References

A.S. Argon, Plastic deformation in metallic glasses. Acta Metall. **27**, 47–58 (1979)

M.F. Ashby, A.L. Greer, Metallic glasses as structural materials. Scr. Mater. **54**, 321–326 (2006)

M. Avella, M.E. Errico, R. Rimedio, PVA/PTFE nanocomposites: Thermal, mechanical, and barrier properties. J. Mater. Sci. **39**, 6133–6136 (2004)

M. Chen, Mechanical behavior of metallic glasses: Microscopic understanding of strength and ductility. Annu. Rev. Mater. Res. **38**, 445–469 (2008)

M. Chiarbonello, D. Firrao, R. Gerosa, A. Ghidini, M.G. Ienco, P. Matteis, et al., Mechanical properties of large plastic-Mold steel blooms. Fracture of Nano & Engineering Materials & Structures, 433–434 (2006)

G. Duan, A. Wiest, M.L. Lind, J. Li, W.K. Rhim, W.L. Johnson, Bulk metallic glass with benchmark thermoplastic Processability. Adv. Mater. **19**, 4272–4275 (2010)

J. Eckert, J. Das, S. Pauly, C. Duhamel, Mechanical properties of bulk metallic glasses and composites. Mrs Bull. **32**, 635–638 (2007)

R.K. Garg, K.K. Singh, A. Sachdeva, V.S. Sharma, K. Ojha, S. Singh, Review of research work in sinking EDM and WEDM on metal matrix composite materials. Int. J. Adv. Manuf. Technol. **50**, 611–624 (2010)

E. Georgatis, A. Lekatou, H. Petropoulos, S. Katsamakis, A. Poulia, Development of a cast Al-MgSi-Si *In Situ* composite: Microstructure, heat treatment, and mechanical properties. J. Mater. Eng. Perform. **22**, 729–741 (2013)

Y. Gong, Y. Sun, X. Wen, C. Wang, Q. Gao, Experimental study on surface integrity of Ti-6Al-4V machined by LS-WEDM. Int. J. Adv. Manuf. Technol. **88**, 1–11 (2016)

X. Gu, W. Hao, J. Wang, H. Kou, J. Li, Microstructure changes in Zr-based metallic glass induced by ion milling. Rare Metal Mater. Eng. **39**, 1693–1696 (2010)

S.F. Guo, Z.Y. Wu, L. Liu, Preparation and magnetic properties of FeCoHfMoBY bulk metallic glasses. J. Alloys Compd. **468**, 54–57 (2009)

M. Heckele, W.K. Schomburg, Review on micro molding of thermoplastic polymers. J. Micromech. Microeng. **14**, R1 (2004)

H. Hu, J. Yan, On the surface characteristics of a Zr-based bulk metallic glass processed by microelectrical discharge machining. Appl. Surf. Sci. **355**, 1306–1315 (2015)

H. Hu, J. Yan, Microstructural changes of Zr-based metallic glass during micro-electrical discharge machining and grinding by a sintered diamond tool. J. Alloys Compd. **688**, 14–21 (2016)

A. Inoue, Stabilization of metallic supercooled liquid and bulk amorphous alloys ☆. Acta Mater. **48**, 279–306 (2000)

W.L. Johnson, G. Kaltenboeck, M.D. Demetriou, J.P. Schramm, X. Liu, K. Samwer, et al., Beating crystallization in glass-forming metals by millisecond heating and processing. Science **332**, 828–833 (2011)

M. Kunieda, C. Furudate, High precision finish cutting by dry WEDM. Ann. CIRP **50**, 121–124 (2001)

J.J. Lewandowski, A.L. Greer, Temperature rise at shear bands in metallic glasses. Nat. Mater. **5**, 15–18 (2006)

G. Liu, P. Gao, Z. Xue, Z. Tong, M. Zhang, Ultra-high strength mg–Li based bulk metallic glasses: Preparation and performance research. Mater. Sci. Eng. A **528**, 7156–7160 (2011)

J. Ma, X. Zhang, W.H. Wang, Metallic glass mold insert for hot embossing of polymers. J. Appl. Phys. **112**(32), 024506 (2012)

S.S. Mahapatra, A. Patnaik, Optimization of wire electrical discharge machining (WEDM) process parameters using Taguchi method. Int. J. Adv. Manuf. Technol. **34**, 911–925 (2007)

L. Mingqi, L. Minghui, X. Guangyao, Study on the variations of form and position of the wire electrode in WEDM-HS. Int. J. Adv. Manuf. Technol. **25**, 929–934 (2005)

P.D. Mitcheson, P. Miao, B.H. Stark, E.M. Yeatman, A.S. Holmes, T.C. Green, MEMS electrostatic micropower generator for low frequency operation. Sensors Actuators A Phy. **115**, 523–529 (2004)

Y. Saotome, K. Itoh, T. Zhang, A. Inoue, Superplastic nanoforming of Pd-based amorphous alloy. Scr. Mater. **44**, 1541–1545 (2001)

J. Schroers, The superplastic forming of bulk metallic glasses. JOM **57**, 35–39 (2005)

W.H. Wang, The elastic properties, elastic models and elastic perspectives of metallic glasses. Prog. Mater. Sci. **57**, 487–656 (2012)

D. Wang, G. Liao, J. Pan, Z. Tang, P. Peng, L. Liu, et al., Superplastic micro-forming of Zr 65 cu 17.5 Ni 10 Al 7.5 bulk metallic glass with silicon mold using hot embossing technology. J. Alloys Compd. **484**, 118–122 (2009)

A. Wiest, J.S. Harmon, M.D. Demetriou, R.D. Conner, W.L. Johnson, Injection molding metallic glass. Scr. Mater. **60**, 160–163 (2009)

Y.M. Yeh, G.C. Tu, T.H. Fang, Nanomechanical properties of nanocrystalline Ni–Fe mold insert. J. Alloys Compd. **372**, 0–230 (2004)

S.H. Yeo, P.C. Tan, E. Aligiri, S.B. Tor, N.H. Loh, Processing of zirconium-based bulk metallic glass (BMG) using micro electrical discharge machining (micro-EDM). Mater. Manuf. Processes. **24**, 1242–1248 (2009)

L. Yi, X. Wang, Y. Fan, Microfluidic chip made of COP (cyclo-olefin polymer) and comparion to PMMA (polymethylmethacrylate) microfluidic chip. J. Mater. Process. Technol. **208**, 63–69 (2008)

N. Zhang, J.S. Chu, C.J. Byrne, D.J. Browne, M.D. Gilchrist, Replication of micro/nano-scale features by micro injection molding with a bulk metallic glass mold insert. J. Micromech. Microeng. **22**, 065019 (2012a)

X. Zhang, J. Ma, R. Bai, Q. Li, B.L. Sun, C.Y. Shen, Polymer micro hot embossing with bulk metallic glass Mold insert. Adv. Mater. Res. **510**, 639–644 (2012b)