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# On the adhesion between metallic glass and dies during thermoplastic forming

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ABSTRACT

Thermoplastic forming (TPF) is an efficient process for the fabrication of metallic glass (MG) components. However, the MG-die adhesion has been one of the crucial issues in the TPF production. This paper presents comprehensive experimental and theoretical studies on the adhesion between two typical MGs (La-based and Zr-based) and various die materials including electroless Ni-P, Si, polytetrafluoroethylene (PTFE), sapphire and SiC. It was found that of the above die materials investigated, PTFE and sapphire were the best in preventing adhesion followed by SiC, electroless Ni-P and Si. Further theoretical prediction also indicated that the work of adhesion of PTFE and sapphire are the lowest among the employed dies, which agrees very well with the experimental results. However, the low melting point of PTFE makes it not a suitable die material for the TPF of some MGs. By considering a number of forming requirements and conditions, this study concluded that sapphire is the best die material for the thermoplastic forming of MG components.

## 1. Introduction

Metallic glasses (MGs) are the alloys which have attracted extensive attention [1–4]. Due to their amorphous microstructure and metallic bonds, MGs possess outstanding characteristics, such as high corrosion and wear resistance, ultrahigh elastic strain limits, high strength and good electrical and magnetic properties [5–7]. These unique properties make MGs a promising class of materials for applications in a variety of areas, including micro-electro-mechanical systems (MEMS), electric transformers and sports elements [8–10]. However, owing to the brittleness and metastable structure, it is difficult to produce complex MG components using conventional manufacturing techniques [11,12].

Researchers have been trying to develop suitable techniques to fabricate cheap but high-quality MG products [11,13]. Casting has been the first and a major manufacturing process in place [1]. However, the requirement of high cooling rate and difficulty in making complex shapes are the barriers to production [6,11]. Machining, which is another widely-used manufacturing process, is not so suitable for the manufacture of MG components, because MGs are hard and brittle with low machinability [14].

On the other hand, the unique super-plasticity of MGs above their glass transition temperature ($T_g$) has made thermoplastic forming (TPF) an ideal technique for the fabrication of MG components. In this way, complex shapes, particularly those of micro and nano-scale products, can be manufactured relatively easily [11,15]. Nevertheless, a precision TPF process has faced new difficulties, one of which is the MG-die adhesion [12,16].

Adhesion plays a major role in several technological applications, ranging from microelectronics and fuel cell to thermal barrier coating and TPF processes [17]. Adhesion between workpiece materials (e.g., glasses [18] and polymers [19–21]) and dies causes the deterioration of the surface quality of products and dies, and has been a major challenge in TPF [19,22]. Some methods have been utilized to separate MGs from dies, such as mechanical separation and dissolution of dies with chemicals [23–26]. Nonetheless, they failed to fully resolve the problem, and often damaged either the MG components or the dies. Due to discontinuity of the physical properties and difficulties associated with experiments, structural and theoretical analyses of the interfaces have been always a challenging issue [17]. Mechanisms and work of adhesion are the major factors giving us valuable information in this area.

MG-die adhesion can be chemical, dispersive or/and diffusive [27], of which the intimate distance between the material pair is a

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critical factor. When an MG is heated to its supercooled liquid region, the material becomes a soft matter because of the dramatic decrease of viscosity. The low viscosity of the MG in this region leads to two key phenomena. First, the atom mobility increases rapidly, which enables them to easily rearrange themselves [28]. Secondly, the inter-diffusion and diffusion coefficients of the MG rise considerably [5]. These cause the MG to be able to wet the surface of another material in the supercooled liquid region [28]. Furthermore, because of the applying load during TPF, the distance between the atoms of the MG and a die surface is significantly reduced, which leads to the intimate contact between the material pair [29,30]. All of these bring out challenges in selecting die materials for TPF of an MG. Wettability has been found to play an important role in adhesion and it is strongly dependent on the surface energy and surface quality of a die material [31]. With increasing the wettability of a die surface, the contact area between an MG and the die extends. Materials with low surface energy, such as ceramics and some polymers [27], are hard to be wet and consequently are difficult to have a chemical reaction with other materials [32].

There exist several models investigating work of adhesion between materials [33,34]. These models are basically based on Dupre equation (equation (1)) and concerned with surface free energy (SFE) of materials and surface interaction of the interfaces [34]. To the best of authors' knowledge, there is not any specific model determined the work of adhesion between MGs and other materials in TPF. Consequently, the growth in the use of MGs in various applications, as well as lack of fundamental knowledge makes adhesion of MGs an essential issue and justifies the demand for further research.

This paper investigates the adhesion behaviour of MGs and some commonly used die materials in TPF. After each TPF, the surfaces of the employed materials will be analysed using optical microscope, SEM, high resolution SEM and EDS. Key material parameters playing important roles will be identified and employed to compare and predict the adhesion status. The SFE of the MGs will also be determined analytically and a model will be presented for calculation of work of adhesion between MGs and different dies in TPF process. Eventually, based on our experimental and analytical analyses, the best die material will be identified.

## 2. Experimental procedure

Two MGs, La-based and Zr-based, were chosen in this study for the investigation of their adhesions with a number of commonly used die materials. The La-based MG, $La_{60.5}Al_{16.3}$ (Cu, Ni)$_{23.2}$, was prepared by arc melting of high purity elements (>99.5%) under the Ti-gettered argon atmosphere, followed by suck casting into copper mould. To produce a homogeneous product, the ingot was remelted several times. The Zr-based MG, $Zr_{58.5}$ $Cu_{15.6}$ $Ni_{12.8}$ $Al_{10.3}$ $Nb_{2.8}$ (LM106a), was purchased from LIQUID METAL TECHNOLOGY. Differential scanning calorimetry (DSC) test was done for measuring the glass transition and crystallization temperatures of the La-based MG by Perkin Elmer DSC 7 at a heating rate of 20 °C/min (Fig. 1a). X-Ray diffraction (XRD) analysis was carried out for verifying the amorphous nature of La-based MG by using Cu $k_{\alpha}$ source (Fig. 1b). For the LM106a, the data supplied by LIQUID METAL TECHNOLOGY was used as a reference. Based on the experiments and the data available, the glass transition and crystallisation of $La_{60.5}Al1_{6.3}$ (Cu, Ni) $_{23.2}$ were determined to be 145 °C and 205 °C, respectively. For the Zr-based MG, these were 395 °C and 499 °C, respectively.

Five widely-used die materials selected in this study were electroless Ni-P, polytetrafluoroethylene (PTFE), Si, sapphire and SiC. It was noted that PTFE and electroless Ni-P were only applicable to La-based MG due to the low temperature required for their thermoforming processes [35].

The electroless Ni-P die used in this study was an amorphous coating with a thickness of 100 μm on copper, fabricated by electroless method. Due to its advanced tribological properties and machinability, electroless Ni-P dies have been widely used in the manufacture of precision products in nano and micro scales [36]. Si dies are among the most popular dies in MEMS and electronic circuit industries, owing to the simplicity of fabricating micro and nano scale features, as well as desirable mechanical and electrical properties [23,25]. In this study Si wafer with around 600 μm in thickness was used as a die material. PTFE is an anti-sticking polymer material, which has a very low surface energy and wettability. In this study, a layer of PTFE with around 100 μm in thickness was coated on copper substrate using PTFE tape. Sapphire and SiC have outstanding tribological properties as a result of their high hardness, high wear resistance and low friction coefficients and thus have a wide range of applications in various industries [37,38]. Thus SiC and sapphire wafers with thicknesses of around 600 μm were also selected for investigation in this study.

The TPF processes were conducted on a Toshiba precision glass moulding machine (GMP-211) in the Nano and Precision Engineering Lab at the UNSW Australia. All of the tests were carried out at a constant moulding temperature (160 °C for La-based and 460 °C for Zr-based MGs) under the moulding load of 200 N and loading time of 180 s. Before the TPF tests, the surfaces of the MG samples were ground and polished to a surface roughness of Ra ~100 nm. After the TPF processes, the adhesion status of the different MG-die material pairs were investigated by means of optical microscope, scanning electron microscope (SEM), high resolution SEM and energy dispersive spectroscopy (EDS).

## 3. Results and discussion

### 3.1. Adhesion status

Table 1 summarises the SFE of dies, moulding temperature and adhesion statues of the employed materials with the MGs after TPF. It can be seen that the selected materials have a wide range of SFE and the extent of adhesion varied significantly among them. PTFE and sapphire showed the best performance against adhesion and electroless Ni-P and Si showed the highest bondability. The status of bondability of SiC was between the former and latter groups. Fig. 2 compares the bonding dissociation energy (BDE) of the primary constituent bonds in each material [39], where the BDE is the energy required for breaking a bond. C-C and C-F are the primary constituent bonds in PTFE; and Al-O, Si-C and Si-Si are the major bonds in sapphire, SiC and Si, respectively. In electroless Ni-P, there are three types of bonds, including Ni-Ni, Ni-P and P-P. Considering the high percentage of Ni (90%) in the material structure of electroless Ni-P, the BDE of Ni-Ni was thus used as the average BDE of the electroless Ni-P in this study. The adhesion results had a very good agreement with the BDE of the primary constituent bonds of the materials, showing that the higher the BDE, the less MG-die adhesion took place. For PTFE which had the highest BDE of the constituent bonds, no adhesion occurred. For the others, bonding area decreased with increasing the BDE. The detailed adhesion behaviour and mechanism of each pair will be discussed in the following sections.

### 3.2. MG adhesion with various die materials

#### 3.2.1. Electroless Ni-P die

Electroless Ni-P is an amorphous material. Due to its excellent wear resistance, it has been used as a die material for the TPF of