PUNCHING SURFACE PATTERNS ONTO ALUMINIUM FOILS USING BMG STAMPS SURFACE-STRUCTURED IN THE SUPER-COOLED LIQUID TEMPERATURE RANGE

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Abstract. Metallic glasses often undergo glass transitions at temperature \( T_g \) well below their crystallisation temperature \( T_c \), and thus possess so-called super-cooled liquid temperature range \( \Delta T = T_c - T_g \) to which they can be heated in principle without crystallization. Metallic glass heated to its \( \Delta T \) regime can be pressed onto a warm substrate to engrave selected patterns. The metallic glass surface then takes on a surface pattern that is the negative of that on the substrate. Subsequently the initial pattern on the substrate can be reproduced on a third target surface at room temperature by cold pressing (punching) the negative pattern on the metallic glass surface onto the target surface. We report the transfer of arbitrary motifs initially on WC or Ni hard surfaces onto Al thin foils via creation of the negative of the pattern on a metallic glass stamp used for punching.

1. INTRODUCTION

Metallic glasses have high yield strengths at room temperature due to an approximately 2% elastic strain range and thus are much harder than most pure metals such as aluminium and copper. Many metallic glasses also have corrosion and wear resistant surfaces while they are usually of eutectic compositions with low melting temperatures \( T_m \) which facilitates fabrication and processing. Metallic glasses often show transitions at \( T_g \) with \( T_g / T_m > 0.55 \) and \( T_g \) a few degrees to more than 100K below their crystallisation temperatures \( T_c \). They thus possess a so-called super-cooled liquid region \( \Delta T = T_c - T_g \) at temperatures often as low as between 550 and 800K to which they can be heated in principle without crystallization.

Thus, in addition to hardness, bulk metallic glasses (BMGs) have the formability of polymers in their super-cooled liquid region’s temperature window \( \Delta T \) far below the temperature range for Nabarro-Herring-type creep in crystalline materials. This temperature range has therefore been used for shaping and joining metallic glasses or for creating micron or submicron-scale motifs on them.

Die forming was proposed [1,2] for production of amorphous metallic articles such as golf club heads by thermo-mechanical processing at temperatures between \( T_g \) and \( T_x \). Electromechanical shaping using Joule heating was applied [3-6] for shaping, joining, forming complex shapes, welding and engraving, by taking advantage of the high electrical resistivity \( r \) of bulk metallic glasses. Lithographic techniques were used to create submicron motifs on metallic glass surfaces [7,8]. Micro-replication was also obtained by hot pressing in the super-cooled liquid region on silicon wafers [9].

Thus one can press a metallic glass heated to its \( \Delta T = T_x - T_g \) regime onto a hot surface with a
certain surface pattern [10]. The metallic glass surface will then show a surface pattern that is the negative of that of the substrate. Subsequently this pattern can be reproduced on a third target surface at room temperature by cold pressing the negative pattern on the metallic glass surface onto the target surface.

In the present work we have used arbitrary motifs initially on WC or Ni hard surfaces to engrave patterns onto BMGs to transfer such motifs onto Al thin foils by punching the Al foils using the engraved BMG as stamp.

2. EXPERIMENTAL

Pd₄₀Cu₃₀Ni₁₀P₂₀ BMG was prepared after liquid alloy fluxing using B₂O₃ slag followed by water quenching inside a quartz tube sealed under vacuum. The BMG pieces were then heated to approximately 653K which is above \( T_g = 580K \) and pressed onto various substrates with some surface micro-patterns using an effective applied pressure \( \tau_{app} \) of about 4 MPa over a time of the order of a few seconds in a chamber mounted on a press as shown in Fig. 1. The chamber was under a vacuum of \( 10^{-3} \) Torr.

The BMG was then quenched via conduction through its contact surfaces with the substrate and the plunger using water circulation to cool the substrate and the plunger. At all stages the glassy nature of BMG pieces which were repeatedly used in this process was tested by X-ray diffraction. Evidence of surface crystallisation was found on the BMGs after the 4th time they were used to forge a stamp (in the super-cooled liquid temperature range) in the press chamber. Pure aluminium
sheets with yield strength of about 70 MPa were then punched by the BMG to replicate the initial substrate surface structure onto the Al sheet. The punching was done with an applied stress of about 120 MPa. The extent of replication of the substrate surface patterns onto the Al sheets was examined by optical microscopy with interferometry and by scanning electron microscopy SEM.

3. RESULTS

Fig. 2 shows the super-position of optical images of the surface morphology initially on a WC substrate first engraved as negative on the BMG stamp, then punched onto the stamped Al sheet. It is seen that the patterns are well replicated from the WC onto the Al sheet. No particular difference was observed in the quality of the replication due to wear after 15 such punchings at 120 MPa.

The resolution in the optical images (Fig. 1) is about 10 µm and only two dimensional, so interferometry was used to get higher resolution and 3-d topology of the initial pattern on the WC substrate and the corresponding pattern replicated on the Al sheet.

Fig. 3 compares the interferometer 3-d topology of the WC substrate and the Al sheet after punching by the BMG stamp.

The lateral resolution in Fig. 3 is of the order of 2 µm and it can be seem that the topologies are identical at that scale on the convex areas but the replication is not good in the concave areas, as can be seen in the flat areas on the Al sheet.

WC was selected because it has very high melting temperature $T_m$ and W is immiscible with Pd and Ni and no interfacial reaction occurs when the BMG stamp is forged on it in the super-cooled liquid region $\Delta T = T_x - T_g$ below 700K. However, the extreme immiscibility may also reduce wetting due to very high interfacial energy at the WC-BMG interface and this may explain the imperfect replication of the WC topology onto the stamped Al sheet.

To improve wetting and better engraving of substrate patterns on the BMG stamp, Ni was next used as substrate. Experimental precautions had to be taken for the Ni substrate not to be heated excessively by the induction coil in the press chamber of Fig. 1 in order to avoid formation of interfacial reaction layers on the forged BMG stamp which lead to welding and destruction of the engraving upon forced separation.

The SEM images of Fig. 4 compare the surface morphology of the Ni substrate with that of the BMG stamp forged on it. It can be seen that the replication is near perfect and more particularly extends to sub-micron scale.

4. DISCUSSION

While replication of the micro-morphology of the WC substrate onto Al sheets punched by BMG stamps engraved by hot pressing onto the WC substrate was obtained, the quality of the engraving was not good on the concave parts of the morphology.
During micro-forging, the stress $\tau_{\text{appl}}$ applied to the super-cooled liquid state to force it into cavities of curvature $r$ is resisted by the force needed to create additional BMG surface with surface energy $\gamma_{\text{BMG}}$. This results in a thermodynamic stress of magnitude $\tau = 2\gamma_{\text{BMG}}/r$ where the super-cooled liquid surface energy $\gamma_{\text{BMG}}$ is about $10^{-4}$ J/cm$^2$ [11] for an order of magnitude calculation. Using $r_{\text{BMG appl}} = 2\gamma_{\text{BMG}}/\tau_{\text{appl}}$, (1) yields that we should be able to curve the super-cooled liquid to curvatures $r \approx 500$ nm which is clearly not the case for the Pd-based super-cooled liquid when pressed onto the fine-scale morphology of the WC substrate (see Fig. 3).

WC was initially selected because of its very high melting temperature $T_m \geq 3000$K. For this fact and W being highly immiscible with Pd and Ni, no interfacial reaction was expected when the BMG stamp is forged on it in the super-cooled liquid region $\Delta T = T_s - T_g$ below 700K. It is thought that the extreme immiscibility leads to very high interfacial energy at the WC - PdNiCuP interface and this can explain the imperfect replication of concave areas of the WC micron-scale surface topology (Fig. 3) onto the stamped Al sheets.

For the sake of discussion, consider a model W/Pd interface. The interfacial energy $\sigma_{\text{interface}}$ neglecting curvature effects, consists of a structural and a chemical component as in the zero-layer model of Becker [12]:

$$\sigma_{\text{interface}} = \sigma_{\text{str}} + \sigma_{\text{chem}} = \left( x_W \cdot \sigma_{\text{str}}^W + x_{\text{pd}} \cdot \sigma_{\text{str}}^\text{pd} \right) + m\Omega / A_{\text{int}},$$

(2)

where $x_W$ and $x_{\text{pd}}$ are the component atomic fractions of the interface area, $m$ is a geometric factor of the order of 0.25 and $\Omega = \Delta H_{\text{mix}} / x_W x_{\text{pd}}$ is the molar exchange energy as in the regular solution model for molar heat of mixing $\Delta H_{\text{mix}}$. The structural component $\sigma_{\text{str}}$ is essentially due to topological disorder and atom-density deficit at the interface and is always positive while the chemical com-
ponent $\sigma_{\text{chem}}$ which accounts for hetero-atomic interactions at the contact surface is negative for alloying elements with negative heats of mixing $\Delta H_{\text{mix}}$ and results in a reduction of the total interfacial energy below $\sigma^{\text{int}}$.

However, in immiscible systems such as W-Pd where hetero-atomic interactions are repulsive, $\Delta H_{\text{mix}} >> 0$ and $\sigma_{\text{chem}} - m\Omega/A > 0$ contributes to significantly increase the interfacial energy $\sigma^{\text{int}}$ at the W/Pd interfaces. A less extreme but nevertheless analogous situation is expected for the interfacial energy at the WC-PdCuNiP BMG interface during forging. When the WC substrate is replaced by a Ni substrate which is easily wetted by the Pd-based BMG the W/Pd interfaces. A less extreme but nevertheless analogous situation is expected for the interfacial energy at the WC-PdCuNiP BMG interface during forging. When the substrate-BMG stamp wetting and the transfer of the substrate does not support shear.

For the above reasons, the substrate-BMG stamp wetting and the transfer of the substrate morphology onto the BMG stamp is much improved when the WC substrate is replaced by a Ni substrate which is easily wetted by the Pd-based BMG containing 10% Ni (seen in the SEM images of Fig. 4).

In conclusion, the feasibility of forging BMG stamps on substrates with various surface morphologies in view of replicating those morphologies onto Al sheets by cold punching has been validated. When the substrate is properly wetted by the BMG during forging in the super-cooled liquid temperature range $\Delta T = T_s - T_g$, the BMG stamps are of excellent quality with perfect engraving of the substrate patterns down to submicron scale. Further characterization is needed to establish the extent of replication in the nanometer range.

REFERENCES