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Accessing thermoplastic processing windows in metallic glasses using rapid capacitive discharge

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The ability of the rapid-capacitive discharge approach to access optimal viscosity ranges in metallic glasses for thermoplastic processing is explored. Using high-speed thermal imaging, the heating uniformity and stability against crystallization of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ metallic glass heated deeply into the supercooled region is investigated. The method enables homogeneous volumetric heating of bulk samples throughout the entire supercooled liquid region at high rates ($\sim 10^5$ K/s) sufficient to bypass crystallization throughout. The crystallization onsets at temperatures in the vicinity of the "crystallization nose" were identified and a Time-Temperature-Transformation diagram is constructed, revealing a "critical heating rate" for the metallic glass of ~1000 K/s. Thermoplastic process windows in the optimal viscosity range of 10^0–10^4 Pa·s are identified, being confined between the glass relaxation and the eutectic crystallization transition. Within this process window, near-net forging of a fine precision metallic glass part is demonstrated.

Since their discovery, one of the most intriguing features of metallic glasses has been their ability to be formed "thermoplastically" above the glass transition temperature. This "thermoplastic forming" ability was widely perceived as finally bridging the gap between the manufacturing of metals and that of plastics and oxide glasses. Metallic glasses are kinetically frozen supercooled liquids, and thus can be heated above their glass transition temperature where they can relax and recover the properties of the metastable liquid. Since glass-forming liquids have a well-defined equilibrium viscosity that depends strongly on temperature, it was thought to be possible to "dial in" to a viscosity simply by equilibrating the liquid at a certain temperature. As known from plastics processing, the optimum viscosity range for thermoplastic forming is typically 10^0–10^4 Pa·s[1], which for metallic glasses implies a processing temperature in the supercooled liquid region well above the glass-transition temperature T_g (where the viscosity is on the order of 10^{12} Pa·s) and also substantially above the crystallization temperature T_x (where the metallic glass crystallizes when heated at a rate of ~1 K/s).

Thermoplastic forming of metallic glass was first proposed by Saotome et al., who reported micro-forming a metallic glass in the supercooled liquid region between T_g and T_x to produce micro-electro-mechanical components[2–7]. Following Saotome's approach, other authors exploited conventional thermoplastic methods used in the processing of plastics and conventional oxide glasses, such as blow molding[8] and injection molding[9], to process bulk articles. Theoretical approaches have also been conceived aiming to quantify the thermoplastic formability of metallic glasses between T_g and T_x[10–12]. These theoretical approaches are based on estimates of the flow capacity between T_g and T_x and involve integration of the viscosity function within that range. They essentially assume that flow would initiate at T_g and terminate at T_x, thereby rendering the difference $\Delta T = T_x - T_g$ a key parameter in quantifying formability. These models have inspired scientists to develop new bulk-glass forming alloys that demonstrate higher and higher ΔT in the hope of further improving metallic glass formability to levels comparable to plastics or conventional oxide glasses[13]. But even metallic glasses with very high ΔT values (as high as 165 K)[14] have viscosities at T_x not lower than 10^6 Pa·s, i.e. still considerably higher than the optimum "thermoplastic" range. Unlike covalently and polymerically bonded glasses (e.g. silicates and plastics), metallic glasses are inherently unstable against crystallization; their centrosymmetric metallic bonding causes them to crystallize rather rapidly when the viscosity drops below 10^6 Pa·s. These limitations are well quantified by the "thermoplastic formability" models[10–12].

To work around these limitations and enable access to the optimum thermoplastic viscosity range 10^0–10^4 Pa·s, the metallic glass must be heated extremely rapidly to temperatures high enough in the undercooled

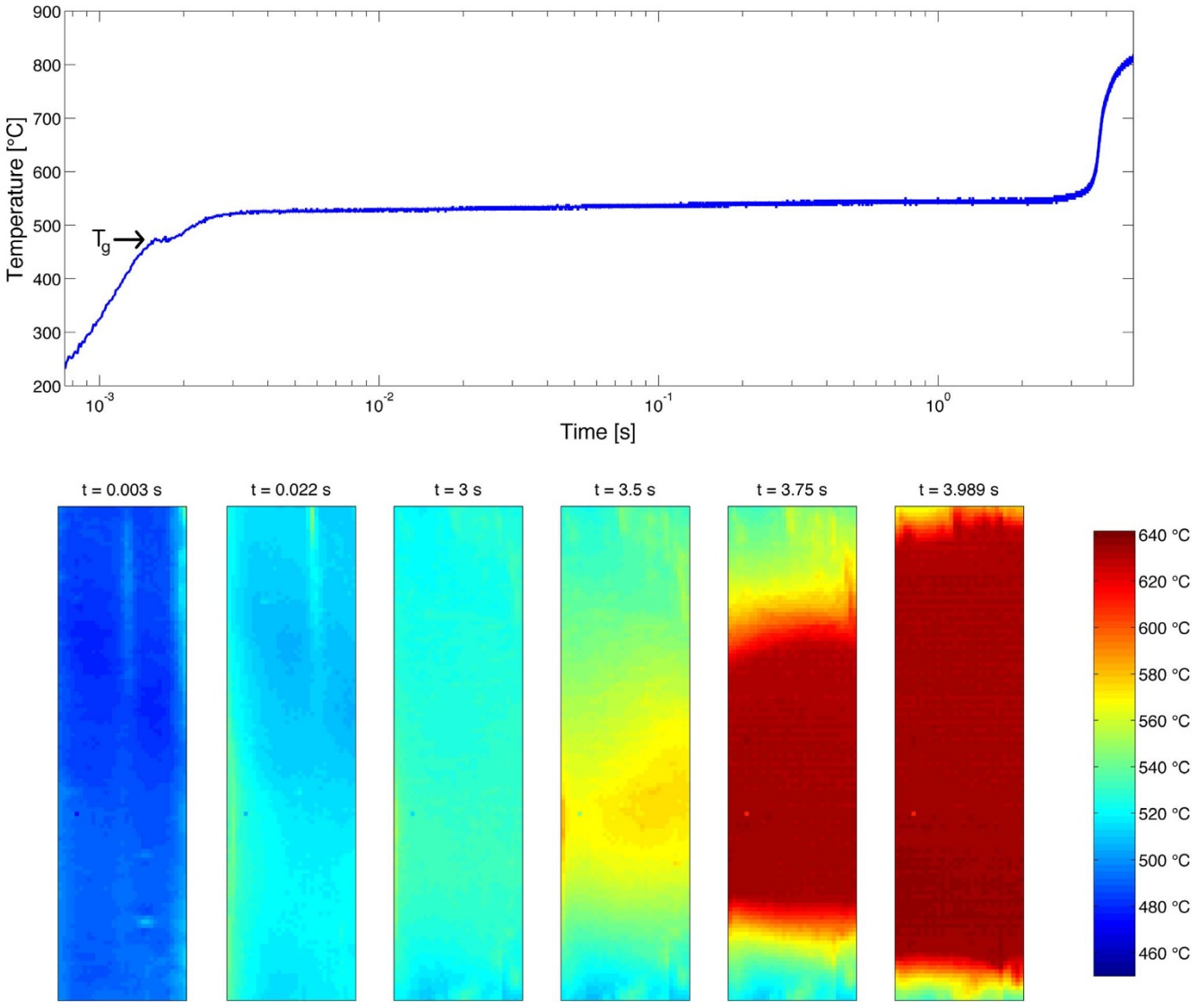

Figure 1 | Local temperature response (A) and distribution of heating evolution at various times (B) of an ohmically heated $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ metallic glass rod. The arrow at the response curve designates the glass-transition temperature.

liquid region on a time scale much shorter than that associated with the onset of crystallization. Preferably, the heating rate utilized must be high enough to suppress crystallization throughout the undercooled liquid region. For typical bulk-glass formers, the "critical heating rate" to bypass crystallization by heating through the entire undercooled region (i.e. from T_g to the melting point) is known to be on the order of 10^4 K/s [15], and can be as low as $\sim 10^2$ K/s for very robust glass formers[16]. But conventional heating methods, where heat is introduced at the boundaries, are incapable of heating the entirety of bulk-glass samples at such high rates due to a sluggish thermal relaxation. Consider for example an amorphous rod with diameter $d = 0.5$ cm and thermal diffusivity $\alpha = 0.03$ cm^2/s (typical for metallic glasses) heated very rapidly over a surface skin (e.g. by high frequency induction). The relaxation time would be $\tau = (d/2)^2/\alpha \sim 1$ s. Hence, to raise the centerline temperature by $\sim 10^2$ K the heating rate would be of order 10^2 K/s regardless of how rapidly the surface is heated. Such a heating rate is significantly lower than "critical heating rates" for typical glass formers, and barely on the order of those for very robust bulk-glass formers. Therefore, 5-mm diameter rods of typical bulk-glass formers would crystallize at the core (and eventually throughout) irrespective of how rapidly their surface is being heated, while 5-mm diameter rods of very robust bulk-glass formers may remain marginally amorphous or barely crystallize.

Recently, a Joule heating approach has been introduced by Johnson et al[17] that generates heat "volumetrically" through a metallic glass such that it overcomes the limitations imposed by thermal relaxation. In this approach, electrical current generated by discharging a capacitor across the sample passes uniformly through the sample enabling heating of the sample homogeneously throughout via dissipation of electrical energy. Since heating is volumetric, the transient temperature distribution is essentially homogenous and free of any gradients. Consequently, the sample is heated homogenously at a rate governed by the internal time constant of the electrical discharge circuit, i.e. by the current rise time. As such, the rate of homogeneous heating of a metallic glass can be controlled almost entirely by the parameters of the electrical circuit, i.e. by the capacitor discharge time constant. Capacitor discharge time constants can be varied enormously over many orders of magnitudes, covering ranges from microseconds to seconds. This allows a broad range of homogeneous heating rates that could be applied to entirely bypass crystallization (i.e. exceed critical heating rates) in a broad range of metallic glasses, from marginal glass formers to highly robust bulk-glass formers. Therefore, by properly designing the capacitor dis-

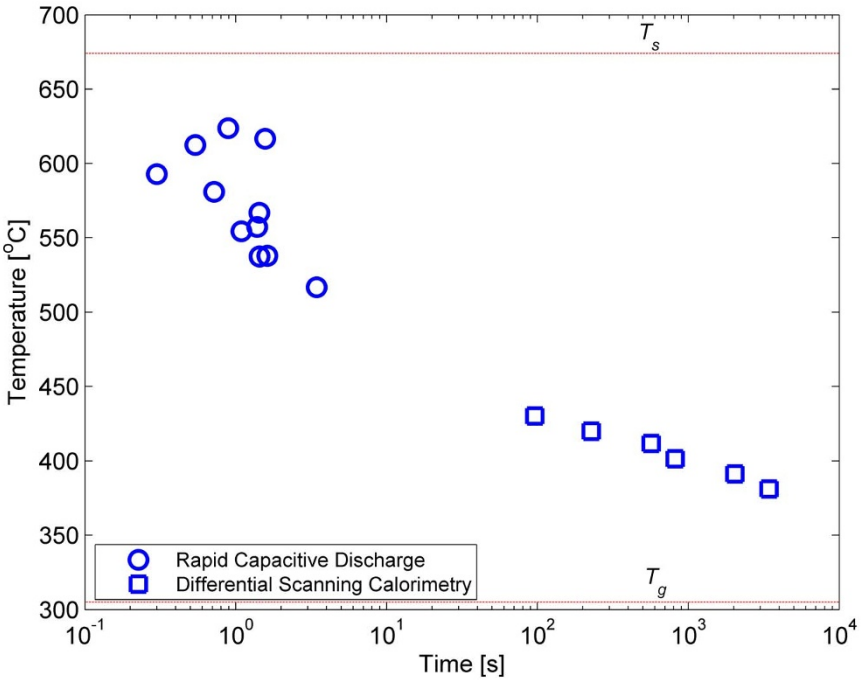

Figure 2 | TTT diagram on heating of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ metallic glass. High temperature data were obtained by rapid capacitive discharge heating (present work), while low temperature data were gathered using differential scanning calorimetry[13].

charge characteristics, the entire undercooled liquid region of a metallic glass could be accessed for processing independent of the glass stability against crystallization, where any desired viscosity (e.g. in the range of 10^0–10^4 Pa·s) can be "dialed in" simply by selecting a discharge voltage. This is a powerful method that has the potential to entirely overcome the limitations imposed by the rapidly intervening crystallization during heating of metallic gasses.

In the work by Johnson et al.[17] it was demonstrated that the rapid capacitive discharge heating method enables near-net thermoplastic shaping by injection molding. In the current work we use $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ as a model bulk-glass former to explore the thermoplastic process window throughout the undercooled liquid region. Specifically, we employ high-speed infrared thermography and pyrometry to track the evolution of temperature distribution in ohmically heated bulk samples, and accurately assess process windows defined between glass transition and crystallization by identifying the signatures for glass relaxation and liquid crystallization.

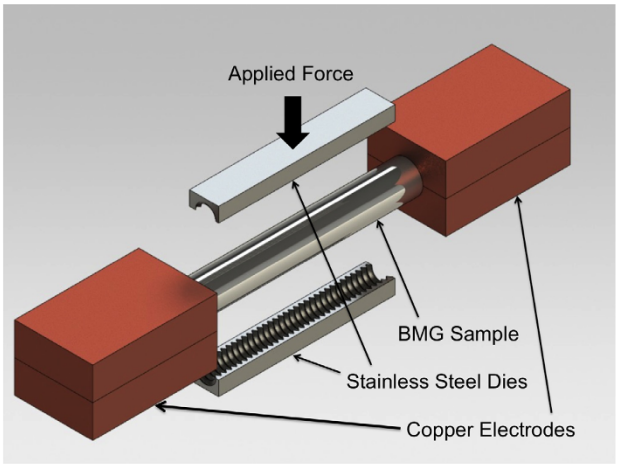

Figure 3 | Schematic of the capacitive- discharge forging configuration, showing the die, electrodes, and metallic glass sample.

By plotting the onsets of crystallization at the various temperatures in the undercooling region, the TTT diagram on heating is constructed. Lastly, thermoplastic forming by near-net forging in the optimum viscosity range of 10^0–10^4 Pa·s is presented.

The temperature history and heating evolution in $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ rods and strips undergoing ohmic heating at various discharge voltages were monitored by a high-speed pyrometer and a high-speed infrared imaging camera. The temperature history and heating evolution in the rod at a discharge voltage of 131.4 V associated with an energy density of 1883 J/cc is presented in Fig. 1. In Fig. 1A, the local temperature response reveals a heating rise time of about 2 ms, over which the heating process saturates as the current pulse fades and the temperature stabilizes at about 530°C. At this temperature the liquid viscosity is anticipated to be about 10^2 Pa·s[13]. The signature of a dynamic glass transition is revealed at approximately 475°C, which is 170°C higher than the calorimetric glass transition (measured at 20 K/min) for this glass[13]. This is a consequence of a very high heating rate, estimated to be of order 10^5 K/s. Following the cessation of heating at 530°C, the temperature appears to remain fairly stable for a period of about 3 s. Just after 3 s a fairly sharp recalescence event is evident in the pyrometer trace, as the sample begins to crystallize at the monitored location. In Fig. 1B, these events are revealed over a spatial range in the rod. During heating as well as after the heating process saturates, the temperature appears fairly uniform and stable across the entire domain monitored. Uniform and stable temperature persists for a period of up to 3 s, beyond which a "nucleus" of heat evolves at the core of the sample, which rapidly spikes to over 640°C while it propagates outwards to consume the entire sample at a speed on the order of ~1 cm/s. The sharpness of the recalescence event, which is consistent with that seen in scanning calorimetry[13], suggests that the liquid crystallizes by coupled eutectic growth. From Figs. 1A and 1B therefore, a "thermoplastic process window" of about 2–3 s at 530°C is revealed where the liquid viscosity is expected to be about 10^2 Pa·s.

The temperature-time crystallization onsets in the ohmic heating experiments performed at various discharge voltages over multiple samples were determined using the slope intercept method and are plotted in Fig. 2. The onsets obtained for the same glass at lower

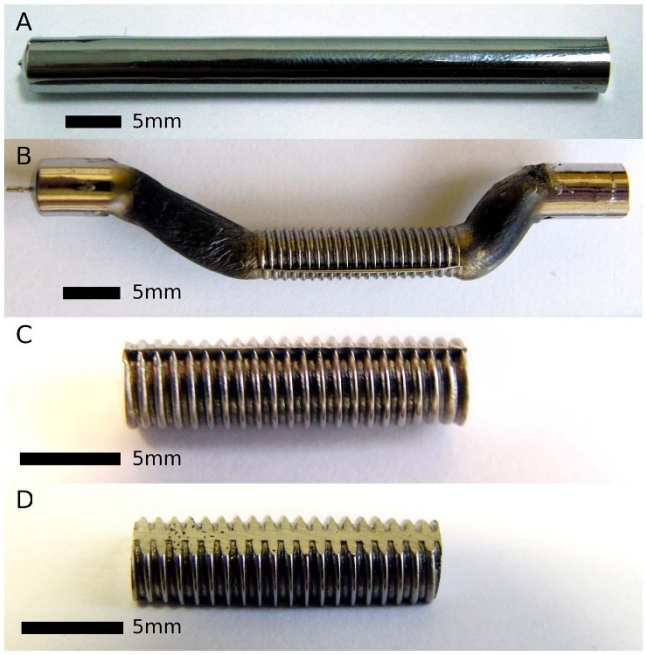

Figure 4 | Images of a $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ metallic glass feedstock rod (A), an as-processed metallic glass sample (B), a forged metallic glass screw part (C), and a post-processed metallic glass screw part (D).

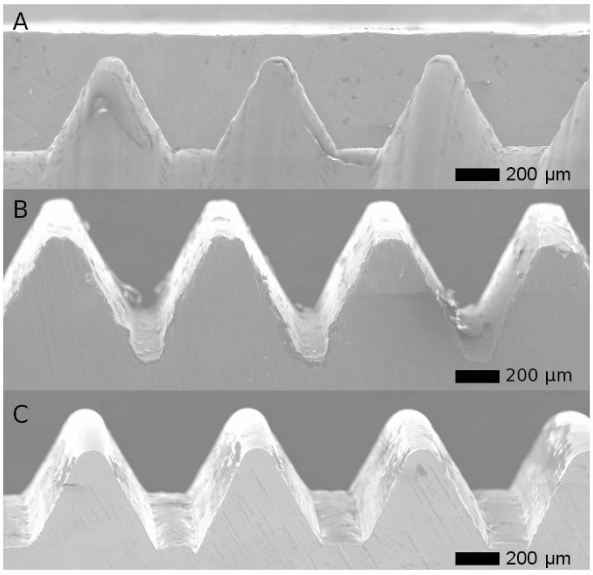

Figure 5 | Scanning electron micrograph of the threads on a standard 10–32 steel screw (A), on the forging die (B), and on the forged metallic glass screw (C).

temperatures and longer times using differential scanning calorimetry[13] are also superimposed in the plot of Fig. 2. Figure 2 represents a TTT diagram associated with the heating a metallic glass spanning across the entire undercooled liquid region, and is the first such diagram studied using thermally equilibrated bulk samples. Previous attempts either utilized uniform heating of micrometer-thick ribbons[15], or involved surface heating of bulk samples[16]. A "critical heating rate" of ~1000 K/s can be estimated from the TTT diagram, associated with a "nose" temperature of 593°C and a "nose" time of 0.3 s. Circling back to the discussion on thermal relaxation, the critical heating rate of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ is considerably higher than the centerline heating rate in a surface-heated 5-cm rod which would be limited by thermal relaxation. This suggests that a 5-cm rod of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ glass heated rapidly at the surface would likely crystallize before or right after it accesses the optimum viscosity range for thermoplastic processing.

To demonstrate the potential of the rapid capacitive discharge method for thermoplastic processing, a near-net forging operation is attempted within the thermoplastic process window identified near 530°C. Unlike injection molding, where the electrodes also act as plungers[17], in forging the ohmic heating process is decoupled from the shaping process, with the forging dies operating independently from the electrodes. The process is presented schematically in Fig. 3, which illustrates forging a screw from a metallic glass rod. The rod is ohmically heated via the electrodes, while the forging dies subsequently (while the rod remains at the process temperature) apply a deformational force to shape the rod into a screw while simultaneously quench the sample to revitrify it.

Forging of a 5 mm amorphous $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ rod (shown Fig. 4A) into a threaded screw is performed using process conditions similar to those that gave rise to the process window around 530°C. A digital image of the as-processed rod is shown in Fig. 4B. The screw component of the rod that has undergone forging is the part in the middle. The unforged part of the rod that has free cooled in air shows significant oxidation, however, the forged part visibly appears entirely free of oxidation. Using x-ray diffraction it was also verified that the forged part is entirely amorphous. The sectioned forged screw part is presented in Fig. 4C, while Fig. 4D shows the screw with the flashing removed. To examine the near-net forging precision, the threads were imaged with scanning electron microscopy. In Fig. 5A, the threads on a standard steel 10–32 screw is presented. The threads on the forging die are presented in Fig. 5B while the threads on the forged metallic glass screw are presented in Fig. 5C. As can be seen, the forged metallic glass screw has finely replicated the die, and the threads closely match those of the standard steel screw.

In conclusion, the rapid capacitive discharge heating method is demonstrated here to be a powerful method capable of overcoming the shortcomings of metallic glasses in thermoplastic processing. Specifically, the method is capable of applying homogeneous heating rates that could entirely bypass crystallization in a broad range of metallic glasses, from marginal glass formers to highly robust bulk-glass formers, enabling access to the entire undercooled liquid region where any desired viscosity could be "dialed in" for thermoplastic processing. Lastly, the application of the rapid discharge heating process for near-net shape processing of metallic glasses presented can have a profound impact on the commercialization and overall technology scale-up of metallic glasses. The demonstrated ability to thermoplastically process a very high strength metal into high-precision near-net shapes is already quite an achievement, as was highlighted in prior literature[1–9]. But the ability to conduct such thermoplastic processing in open air over millisecond timescales using shaping pressures comparable to those used in the processing of plastics, and at temperatures below typical tempering temperatures for conventional tooling, as demonstrated here, represents a significant technological leap forward.

Methods

To generate the heating curves, amorphous $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ rods 5-mm in diameter 5-cm in length and strips 1-mm in thickness, 7-mm in width and 4-cm in length were prepared by arc-melting in a water-cooled copper hearth under inert atmosphere followed by suction casting in a copper mold. A high speed infrared imaging camera (FLIR Corp., SC2500) with a spectral band from 0.9 to 1.7 μm outfitted with a bandpass filter allowing wavelengths from 1.5 to 1.9 μm was employed at frame rates of 250–994 frames/s to record the evolution of temperature distribution. An IMPAC IGA740-LO high-speed infrared pyrometer with a spectral band from 1.58 to 2.2 μm and a response time of 6 microseconds was also used to record temperature vs. time over a circular focal spot of ~1 mm diameter near the rod center. Both camera and pyrometer were calibrated simultaneously by tracking the melting of $Pd_{43}Ni_{10}Cu_{27}P_{20}$ alloy with a solidus temperature of 531°C, which is within the temperature range considered in this work. Using this method, emissivities of 0.285 and 0.26 were found for the infrared camera and pyrometer, respectively. The

emissivities are believed to be roughly representative of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ and that the temperature error is expected to be limited to within $\pm 20^{\circ}C$. Ohmic heating of the amorphous $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ samples was performed using a 0.264 F capacitor bank with a current rise time of about 1 ms was used at voltages ranging between 40–140 V.

For the forging operation, a split die was fabricated from stainless steel with half of a 1.8 cm long 10–32 thread on each side. A 5 mm amorphous $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ rod prepared as described above was placed between the dies and held in place with copper leads. A 0.792 F capacitor bank was charged to 94 V depositing 2080 J/cc of electrical energy into the sample with a current rise time of about 10 ms. The initiation of the capacitive discharge is detected by a sensor circuit measuring current in a portion of the discharge circuit. The detection of discharge activates a pneumatic valve to apply a force of 3 kN to the softened metallic glass via a pneumatic piston. A delay of approximately 10 ms occurs between the activation of the valve and contact between the die and the sample, due to mechanical constraints of the piston. The process was performed in open air.

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Author contributions

G.K. and J.P.S. conducted the kinetic experiments and imaging analysis, G.K., T.H., K.S., T.T. and G.C. conducted the forging experiments, G.K., M.D.D. and W.L.J. wrote the main manuscript.

Additional information

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