Science Bulletin 69 (2024) 163–166

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Short Communication

Ultrasonic vibration enabled under-liquid forming of metallic glasses

Xin Li [a], Luyao Li [b], Sajad Sohrabi [b], Jia'nan Fu [c], Zhen Li [c], Zhe Chen [b], Rongce Sun [b], Yu Zhang [b], Jinbiao Huang [b], Heting Zhang [b], Jian Zhu [b], Xiangyan Chen [d], Kaikai Song [a,d,*], Jiang Ma [b,*]

[a] School of Mechanical, Electrical & Information Engineering, Shandong University, Weihai 264209, China
[b] State Key Laboratory of Radio Frequency Heterogeneous Integration, College of Mechatronics and Control Engineering, Shenzhen University, Shenzhen 518060, China
[c] Department of Mechanics and Aerospace Engineering, Southern University of Science and Technology, Shenzhen 518055, China
[d] Shenzhen Research Institute of Shandong University, Shenzhen 518057, China

ARTICLE INFO

Article history:
Received 10 October 2023
Received in revised form 7 November 2023
Accepted 21 November 2023
Available online 29 November 2023

Advancements in forming technology offer significant advantages for the manufacturing industry, including enhanced efficiency, energy conservation, and improved material utilization [1]. However, traditional additive manufacturing [2], thermoplastic forming [3], and laser cutting [4] encounter challenges when applied in under-liquid environments, mainly due to difficulties in temperature control and heat source provision.

Alternative methods like underwater arc welding and underwater laser beam welding have proven effective for repairing marine equipment and offshore oil production machinery. Nevertheless, these approaches generate elevated temperatures, which can compromise the quality and functionality of the repaired components. Additionally, risks such as phase transformations, softening, creep, thermal expansion, and increased currents pose concerns for builder safety [5]. To address these challenges, further research and development are essential to enhance the accuracy and reliability of under-liquid repair methods while mitigating the risk of overheating.

It is crucial to highlight that existing under-liquid processing technologies are primarily tailored for underwater environments and may not be suitable for tasks involving flammable liquids or extreme low-temperature conditions. Moreover, the demand for corrosion-resistant, robust, high-strength materials capable of adapting to varying temperatures and pressures in underwater environments serves as a hindrance to the advancement of underwater forming technology.

Bulk metallic glasses (BMGs) possess outstanding properties for marine engineering applications but are often challenging to form due to inherent limitations in plasticity and susceptibility to high-temperature failure [6]. A novel approach known as ultrasonic vibration-induced plasticity (UVIP) has emerged as an innovative strategy to overcome these challenges and enhance the formability of BMGs [7].

UVIP has demonstrated success in various applications, including welding [6,8], punching [9], and extrusion molding [10] of BMGs. This technique offers notable advantages, such as reduced processing time, avoidance of temperature elevation, and stress reduction [7]. In essence, ultrasonic vibration proves to be a promising catalyst for the development of under-liquid forming (UUF) techniques, ensuring the preservation of material properties and contributing to the extended service life of components. The impact of this advancement is noteworthy, encompassing applications in both deep-sea and deep-space environments.

Based on the above findings, a novel process for forming BMGs in a liquid environment is proposed, as illustrated in Fig. 1a. Concurrently, ultrasonic vibration is generated from an ultrasonic horn positioned above. In various liquid environments—freshwater, seawater, alcohol, and even LN2—the BMGs exhibit uniform deformation under the influence of ultrasonic vibration. This method holds promise for *in-situ* robot fabrication in deep-sea environments, presenting potential cost reductions and preserving material properties for advanced robots and their BMG components fabricated under liquid conditions.

Snapshots from a high-speed camera video recorder, depicted in Fig. 1b, d, and f, capture the plastic deformation of Zr-based, Pt-based, and La-based BMGs under seawater. The entire process, as showcased in the Supplementary materials Video (online) for all three environments (except for LN2, which is challenging to observe), occurs in less than 1 s, achieving over 50% plastic deformation of BMGs. This starkly contrasts with the room temperature characteristics of the BMGs, as illustrated in Fig. S1a–c (online), where, in stress–strain curves, all three BMGs exhibit only 2% elas-

* Corresponding authors.
E-mail addresses: songkaikai8297@gmail.com (K. Song), majiang@szu.edu.cn (J. Ma).

https://doi.org/10.1016/j.scib.2023.11.049
2095-9273/

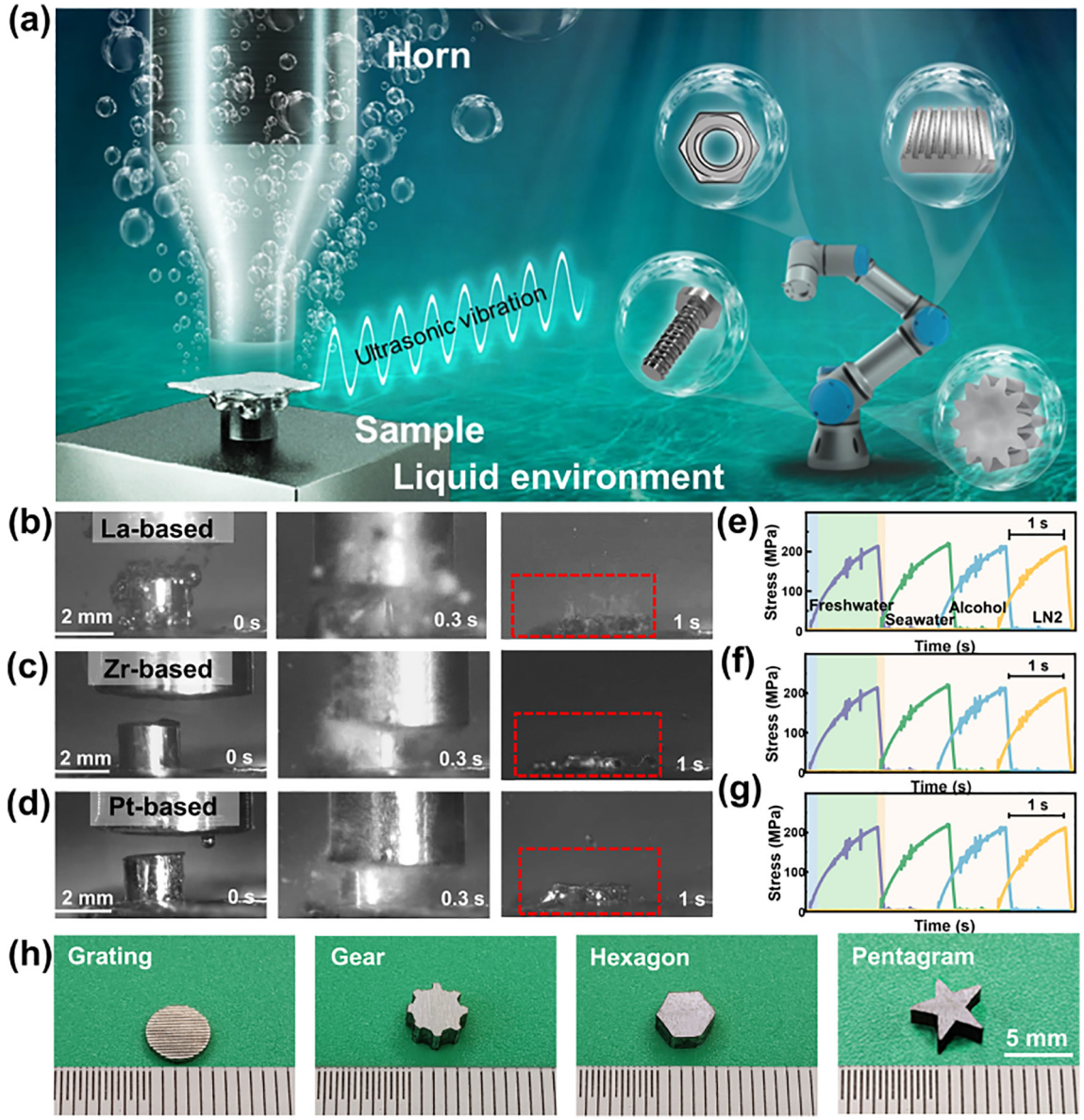


Fig. 1. (Color online) UUF processing of BMGs. (a) Schematic diagram of UUF and prepared components for robot. High-speed imaging of the undergoing UUF of La-based BMG (b), Zr-based BMG (c), Pt-based BMG (d). Real-time collection of stress–strain curves during UUF of La-based BMG (e), Zr-based BMG (f), Pt-based BMG (g). (h) Physical maps of grating, gear, hexagonal, and pentagram that are fabricated by UUF under seawater.

tic strain over approximately 20 s, underscoring the intrinsic brittleness of BMGs. In comparison to quasi-static compression, BMGs demonstrate remarkable plastic deformation when subjected to ultrasonic UUF in various liquid environments.

For a comprehensive understanding of the UUF phenomenon and its potential applications, delving into more intricate details becomes imperative. The stress-time curves of BMGs under UUF, as shown in Fig. 1c, e, and g, have been recorded. The maximum stress of around 200 MPa, a value significantly lower than the compressive strengths of La-BMG (765 MPa), Zr-BMG (1681 MPa), and Pt-BMG (1338 MPa) as can be observed in Fig. S1a–c (online). Temperature data of BMGs were collected during the experiment to investigate their deformation behavior, as shown in Fig. S3 (online). By harnessing the UUF technique, intricate structures of BMGs have been successfully fabricated in liquid environments. Fig. 1h and Fig. S2 (online) illustrate examples of such structures, including grating, gear, pentagram, and hexagonal, obtained under seawater and LN_2 environments, respectively. These images showcase the versatility and adaptability of UUF in creating complex BMG structures even in challenging liquid environments. The notable advantages of this manufacturing process are its extremely short production time (~1 s), low stress and low-temperature rise (20–116 °C, as shown in Fig. S3 online). The resulting material surfaces exhibited a shiny appearance without oxidation or discoloration, indicating the effectiveness of the UUF in preserving the integrity and quality of the BMGs due to insulating the material from the atmosphere. The functional performance of BMGs will be greatly reduced due to crystallization. Thus, characterization of the amorphous state must be utilized to promote effective shaping, while still preserving the amorphous state. As shown in Fig. S4 (online), the amorphous states of BMGs after UUF were characterized and confirmed using X-ray diffraction and transmission electron microscope. These findings indicate that the ultrasonic UUF process has not substantially altered the amorphous properties of the BMGs.

To gain deeper insight into the thermal properties of the BMGs after UUF, additional characterization techniques were used. As expected, the processed BMGs did not manifest significant changes in characteristic temperatures (T_g and T_x) due to the employed processing method, as illustrated in Fig. 2a. However, upon closer examination, the differential scanning calorimetry results for BMGs in the inset of Fig. 2a indicate a significant increase in the heat of excess relaxation enthalpy (ΔH_{rel}) after UUF, and these values also summarized in Fig. 2b and Table S1 (online). For example, the as-cast Pt-based BMG presents a relaxation enthalpy of ~0.22 J/g, and the relaxation enthalpy values and corresponding reductions of La-based BMG after UUF in different environments, including freshwater, seawater, alcohol, and LN_2, are reported as follows: 0.41 J/g (↑ ~0.19 J/g), ~0.53 J/g (↑ ~0.31 J/g), ~0.36 J/g (↑ ~0.14 J/g), and ~0.45 J/g (↑ ~0.23 J/g), respectively. Similarly, the relaxation enthalpy changes of Zr-based and La-based BMG share the same trend, as shown in Fig. S5a, b, and Table S1 (online). And nanoindentation experiments were performed, as depicted in Fig. S5d–f (online), to evaluate the hardness and elastic modulus, as summarized in Fig. 2c and Fig. S5c (online) [11]. The analysis of force–displacement curves for as-cast and UUF-processed BMGs revealed a decrease in the modulus and hardness of processed BMGs. The observed decrease in modulus and hardness lends support to the theory that UUF of BMGs does not induce crystallization but instead initiates rejuvenation [12]. This finding aligns with the consistent results obtained from DSC measurements [7]. It is widely recognized that rejuvenation of BMGs triggers enhanced plastic deformation ability, catalytic activity, and frictional properties [13].

The observed increase in relaxation enthalpy suggests that the BMG undergoes a rejuvenation process, wherein its atomic structure becomes looser after undergoing cyclic stress treatment through UUF. BMG structures consist of both solid and liquid regions, leading to structural heterogeneity [14]. The liquid region undergoes atomic-scale expansion due to cyclic stresses and localized shear events, promoting its activation and expansion [7,15]. As demonstrated in Fig. 2d, the red-colored liquid-like zone rapidly expands and forms after UUF treatment, ultimately connecting with neighboring liquid-like zones. During ultrasonic treatment, the liquid-like zone within MGs increases rapidly, giving it the potential for and plastic deformation rapidly under the pressure of the equipment, gaining the ability to overcome the energy barriers, as shown by "UUFing" state in Fig. 2e. Subsequently, the ultrasonic vibration stops releasing, the liquid-like zone is rapidly reduced and frozen, and part of the liquid-like zone are not transformed in time, resulting in a state with more liquid-like zones and looser atomic structure than the as-cast counterpart, as shown by "post-UUF" state. The softening behavior of the sample is mainly attributed to the intrinsic dynamic heterogeneity of MG and the action of cyclic stress, which leads to atomic-scale expansion and subsequent occurrence of rejuvenation, ultimately resulting in UUF.

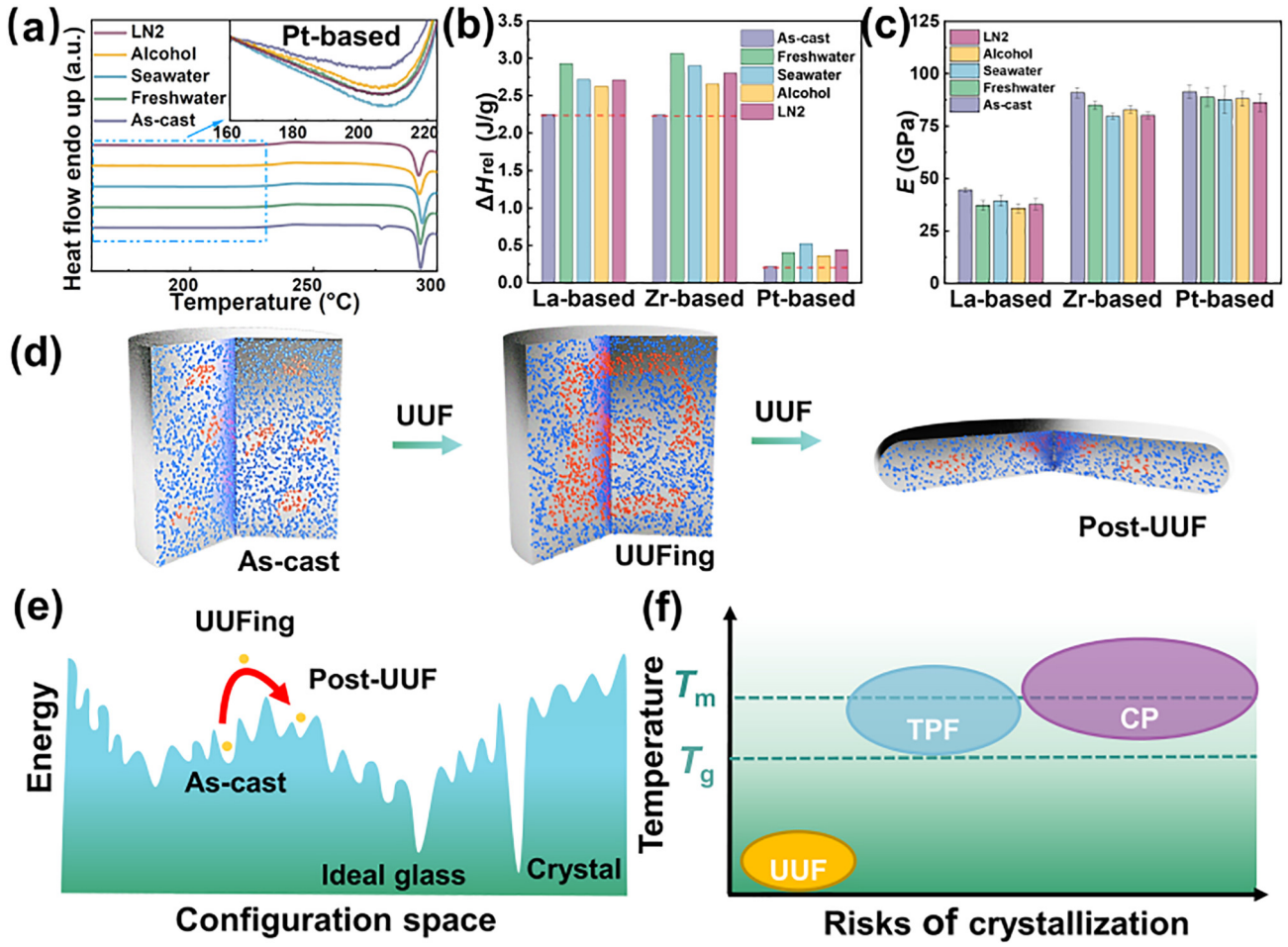


Fig. 2. (Color online) Mechanical, structural characterization, and mechanism of BMGs. The DSC curves of (a) Pt-based BMGs are shown in the figure, with the inset providing a magnified view of the relaxation enthalpy. The relaxation enthalpy of each BMG is summarized in (b). (c) Young's modulus of as-cast and processed BMGs was obtained by nanoindentation. (d) Atomic-scale schematics of the cast, under UUF and post-UUF, where the red atom is liquid-like regions, the blue atom is solid-like regions. (e) Potential energy landscapes of as-cast BMG and after undergoing UUF treatment BMG, along with their respective atomic structures in the inset. (f) A schematic time–temperature-transition diagram that shows the processing methods of UUF, TPF, and CP.

Fig. 2f schematically compares risk of crystallization and temperature during UUF, thermoplastic forming (TPF), and conventional processing (CP). When subjected to liquid environments and ultrasonic vibrations, BMGs showed a temperature significantly below the T_g and underwent rapid processing in less than 1 s, thereby avoiding crystallization. TPF offers a larger processing temperature and time window than CP, but requires careful temperature control to prevent relaxation or crystallization [3,7], as shown in Fig. S6 (online). CP involves heating BMGs above T_m and high cooling speed that significantly affects the amorphous structure and properties of BMGs, leading to a high risk of crystallization. In conclusion, compared with TPF and CP methods, UUF presents a lower risk of crystallization and low temperature ($\ll T_g$) in BMGs. This ability to control crystallization and properties of BMGs effectively makes UUF a promising technique for their fabrication and application.

This research has yielded significant results through the development of processing and forming techniques for BMGs in diverse liquid environments. The heatless processing method demonstrated short processing time (~1 s) and low stress (~300 MPa), overcoming the forming challenges in extreme conditions. The observed rejuvenation phenomenon indicates noteworthy changes in the structure and energy state of the BMGs. In addition, the study successfully fabricated complex structures and components such as gratings, gears, and hexahedrons using the UUF, demonstrating its practicality and flexibility. These findings open up exciting possibilities for efficient processing in liquid environments, with potential applications in aerospace, energy, and marine engineering. These applications include *in-situ* vessel and container repair, polar construction and exploration, deep-sea exploration, providing valuable insights, and paving the way for future advances in submerged processing techniques.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

The work was supported by the Key Basic and Applied Research Program of Guangdong Province, China (2019B030302010), the National Natural Science Foundation of China (52122105, 51971150), the Shenzhen Fundamental Research Program (JCYJ20210324121011031), the Science and Technology Innovation Commission Shenzhen (RCJC20221008092730037 and 20220804091920001), and the National Key Research and Development Program of China (2018YFA0703605). The authors also thank the assistance on microscope observation received from the Electron Microscope Center of Shenzhen University.

Author contributions

Xin Li and Luyao Li conceived the idea and designed the experiments, which was further refined by all authors. Xin Li, Heting Zhang, and Zhe Chen fabricated the materials. Jia'nan Fu, Zhen Li, Rongce Sun, Yu Zhang, Jinbiao Huang, Jian Zhu, and Xiangyan Chen conducted the characterizations. Xin Li analyzed the data and wrote the manuscript. Jiang Ma, Sajad Sohrabi, and Kaikai Song analyzed the separation mechanism and revised the manuscript.

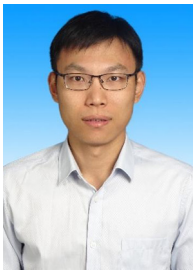
Appendix A. Supplementary materials

Supplementary materials to this short communication can be found online at https://doi.org/10.1016/j.scib.2023.11.049.

References

[1] Yang H, Zhan M, Liu YL, et al. Some advanced plastic processing technologies and their numerical simulation. J Mater Process Tech 2004;151:63–9.
[2] DebRoy T, Wei HL, Zuback JS, et al. Additive manufacturing of metallic components—process, structure and properties. Prog Mater Sci 2018;92:112–224.
[3] Ma J, Yang C, Gong F, et al. Thermoplastic forming of bulk metallic glasses. Acta Phys Sin 2017;66:176404.
[4] Bärsch N, Körber K, Ostendorf A, et al. Ablation and cutting of planar silicon devices using femtosecond laser pulses. Appl Phys A 2003;77:237–42.
[5] Guo N, Fu Y, Wang Y, et al. Effects of welding velocity on metal transfer mode and weld morphology in underwater flux-cored wire welding. J Mater Process Tech 2017;239:103–12.
[6] Li X, Liang X, Zhang Z, et al. Cold joining to fabricate large size metallic glasses by the ultrasonic vibrations. Scripta Mater 2020;185:100–4.
[7] Li X, Wei D, Zhang JY, et al. Ultrasonic plasticity of metallic glass near room temperature. Appl Mater Today 2020;21:100866.
[8] Huang Z, Fu J, Li X, et al. Ultrasonic-assisted rapid cold welding of bulk metallic glasses. Sci China Mater 2021;65:255–62.
[9] Luo F, Sun F, Li K, et al. Ultrasonic assisted micro-shear punching of amorphous alloy. Mater Res Lett 2018;6:545–51.
[10] Ma J, Yang C, Liu X, et al. Fast surface dynamics enabled cold joining of metallic glasses. Sci Adv 2019;5:eaax7256.
[11] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J Mater Res 1992;7:1564–83.
[12] Ketov SV, Sun YH, Nachum S, et al. Rejuvenation of metallic glasses by non-affine thermal strain. Nature 2015;524:200–3.
[13] Pan J, Wang Y, Guo Q, et al. Extreme rejuvenation and softening in a bulk metallic glass. Nat Commun 2018;9:560.
[14] Qiao JC, Wang Q, Pelletier JM, et al. Structural heterogeneities and mechanical behavior of amorphous alloys. Prog Mater Sci 2019;104:250–329.
[15] Chang C, Zhang HP, Zhao R, et al. Liquid-like atoms in dense-packed solid glasses. Nat Mater 2022;21:1240–5.

Xin Li received his Master's degree in Mechanical Engineering from Shenzhen University (SZU) in 2021. He is currently a Ph.D. candidate at School of Mechanical, Electrical & Information Engineering, Shandong University (SDU). His research includes metallic glasses, ultrasonic forming, advanced manufacturing, and metallic glass composites.



Kaikai Song received his Ph.D. degree from TU Dresden/IFW Dresden in 2013. He is currently a professor at School of Mechanical, Electrical & Information Engineering, SDU. His research focuses on metallic glass composites, high-entropy alloys, and their additive manufacturing process.

Jiang Ma received his B.Sc. degree in Materials Science and Engineering from Southeast University in 2009 and Ph.D. degree from the Institute of Physics, Chinese Academy of Sciences (CAS) in 2014. He is currently a professor at College of Mechatronics and Control Engineering, SZU. His research includes metallic glass, high-entropy alloy, micro/nano precision forming, functional surface abrication and application.