

Design of near-zero thermal expansion composites with superior mechanical properties in a wide temperature region



Shike Huang ^a, Fei Sun ^a, Wenqing Ruan ^{a,**}, Shuai Ren ^a, Zhenxuan Zhang ^a, Xiong Liang ^a, Jiang Ma ^{a,b,*}

^a Guangdong Key Laboratory of Electromagnetic Control and Intelligent Robots, Shenzhen University, Shenzhen 518060, China

^b Shenzhen Key Laboratory of High Performance Nontraditional Manufacturing, College of Mechatronics and Control Engineering, Shenzhen University, Shenzhen, 518060, China

ARTICLE INFO

Article history: Received 13 March 2023 Accepted 11 June 2023 Available online 14 June 2023

Keywords: Metallic glasses Near-zero thermal expansion Superior compressive strength Thermal stability

ABSTRACT

Materials that exhibit very small dimensional changes with temperature, i.e., near-zero thermal expansion (NZTE) properties, find attractive prospects in fields such as precision instrumentation and aerospace. However, how to manually design and synthesize NZTE materials with high performance instead of laboriously exploring composition has been a long-standing challenge. In this study, based on the excellent bonding and forming abilities of metallic glass (MG), a composite with continuous regulation of thermal expansion was obtained by combining different volume ratios of MG with beta-LiAlSiO₄ (beta-LAS) possessing negative thermal expansion (NTE). Interestingly, excellent NZTE performance of 0.693 and 1.587 ppm/K was achieved over the 150-700 K temperature range when the volume ratio of MG was 40% and 50%, respectively. In addition, the compressive strength of the NZTE composite reached 320 and 436 MPa for the above two ratios, respectively. The thermal shock resistance results show that the composite can withstand thermal cycling tests of not less than 80 times. The proposed strategy not only provides new NZTE materials with high performance but also facilitates a shift in the preparation of highperformance NZTE composites from laborious search to customizable design. © 2023 The Author(s). Published by Elsevier B.V. This is an open access article under the CC

BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Most objects in nature will expand when heated and contract when cooled, which is also known as positive thermal expansion (PTE) behavior [1,2]. Later, it was discovered that there were materials that contract when heated and expand when cooled; these were known as negative thermal expansion (NTE) materials [3]. The rapid development of society today in the fields of microelectronics, aerospace, and precision instrumentation requires functional components and other materials to face a complex temperature environment;

https://doi.org/10.1016/j.jmrt.2023.06.097

^{*} Corresponding author. Guangdong Key Laboratory of Electromagnetic Control and Intelligent Robots, Shenzhen University, Shenzhen 518060, China.

^{**} Corresponding author.

E-mail addresses: ruanwq@szu.edu.cn (W. Ruan), majiang@szu.edu.cn (J. Ma).

^{2238-7854/© 2023} The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http:// creativecommons.org/licenses/by-nc-nd/4.0/).

thus, the coefficient of thermal expansion (CTE) of a material is particularly critical [4,5]. For example, the Chang'e 5 probe that China launched in 2020 is subject to temperatures on the moon that range from 123 to 453 K ($\Delta T = 330$ K) [6,7], where materials for critical components need to offset the effect of thermal expansion in order to ensure high accuracy and durability. There has been significant effort to investigate the mechanisms of thermal expansion as well as to acquire materials with lower or even near-zero CTE by various means [8-10]. In 1896, C.E. Guialme first discovered the Invar alloy (Fe_{0.64}Ni_{0.36}), which exhibits a low CTE near room temperature (RT) and thus remains dimensionally stable over a range of temperatures, as indicated by Kainuma et al. [11] and Shiga [12]. The property is also known as near-zero thermal expansion (NZTE) or zero thermal expansion (ZTE) [9]. Moreover, materials exhibiting low or even near-zero CTE can ensure the stability of components and precision equipment as well as substantially extend the durability of materials, which shows great promise for applications in microelectronics, aerospace, and precision instrumentation [4,5,13]. Unfortunately, NZTE materials are extremely rare in nature, and most of the existing NZTE materials possess high density, poor mechanical properties, and a narrow temperature range [9,14].

Developing a simple and effective method to successfully obtain NZTE materials showing excellent overall performance is important for solving the above-mentioned problems. The fabrication of the NZTE materials by combining NTE materials with PTE materials is considered a feasible method [15,16]. Materials used in the fabrication of NZTE processes with NTE properties, such as zirconium tungstate (ZrW₂O₈) and beta-LiAlSiO₄ (beta-LAS), function to offset PTE and are thus also known as swelling inhibitors. These selected PTE materials usually enhance certain properties of this NZTE composite; they are also known as reinforcement materials [17,18]. However, one of the major disadvantages of NTE materials is that they tend to undergo phase changes or decomposition when exposed to temperatures or pressures at relatively higher levels [19]. For instance, substantial articles on the fabrication of NZTE materials where ZrW₂O₈ is used as an expansion inhibitor can undergo transition from α to β phase at 428 K [19–22]. In addition, ZrW₂O₈ exhibits low pressure resistance, resulting in a significant decrease in the NTE coefficient due to the transition from cubic phase α to orthogonal phase γ when a pressure of 0.21 GPa is imposed [23-26]. Moreover, the present method of preparation of NTZE typically involves sintering, but the temperature of sintering is usually extremely high and the process is lengthy, which leads to an increased possibility of ineffective swelling inhibitors as well as poor interfacial bonding quality [26-28]. It is noteworthy that previous work on the fabrication of NZTE materials has rarely reported on the mechanical properties and the ability to modulate CTE over a range of temperatures [10,29-34]. Duwez et al. [35] discovered in 1960 a material known as metallic glass (MG), which possesses superior mechanical properties, a relatively low CTE, as well as excellent bonding and molding capabilities [36,37,38]. The MG's unique thermoplastic forming capability allows it to be molded into various complex structures by loading at a certain pressure level in the subcooled liquid region (SLR), where the SLR temperature is usually significantly lower than conventional metals [39-44]. As a result, MG can be bonded

with NTE materials at moderate temperatures [36,45], which will reduce the possibility of failure of swelling inhibitors during the fabrication of NZTE composites and thereby obtain better properties of NZTE composites.

In this work, a universal and effective strategy was provided to successfully fabricate MG matrix composites that exhibit high compressive strength and NZTE over a very wide temperature region while achieving regulation of CTE and compressive strength. To obtain the above NZTE composites, the Zr-based MG powders possessing PTE properties for the reinforcement and adhesive were mixed in various volume ratios with the beta-LAS powders possessing NTE properties. In the whole fabrication process, it benefits from the relatively lower fabrication temperature (~760 K) as well as the faster pressing step (under 1 min), which assures excellent stability of beta-LAS and thus high-performance NZTE composites. By varying the volume ratio of MG and beta-LAS addition, control of CTE and compressive strength for the composites was achieved. When MG was added at volumes of 20%, 40%, and 50%, the composites acquired NZTE properties in the very broad temperature region (150-700 K), showing linear CTE of 0.221, 0.693, and 1.587 ppm/K, respectively. Besides, the compressive strengths of the above three ratios of NZTE composites with increasing ratios of added MG reached 191, 320, and 436 MPa, respectively. Interestingly, the NZTE composites exhibit stable thermal expansion and excellent thermal shock resistance. Benefiting from the excellent thermoforming ability of MGs, various NZTE components were fabricated to demonstrate the excellent shape flexibility and processing capabilities of the NZTE composites obtained from this work.

2. Experimental section

2.1. Materials preparation

The Zr-based MG $Zr_{55}Cu_{30}Ni_5Al_{10}$ (at.%) has been chosen as the PTE material in the fabrication of NZTE composites owing to its wide SLR, excellent flow and molding ability, as well as its mechanical properties at moderate temperatures. The fabrication of Zr-based MG powders can be roughly divided into three steps. The first step was the fabrication of as-cast MG by the traditional water-cooled copper mold casting method; the second step was the fabrication of MG strips by the classical melt-spinning technology; and finally, the MG strips were cut into average-sized particles of about 70 μ m. Based on the strategy of preparing NZTE composites by combining NTE materials with PTE materials, the beta-LAS powder possessing NTE (-6.1 ppm/K) has been selected for the swelling inhibitor [18]. The above beta-LAS powders were purchased directly from Zibo Chendong New Material Co., Ltd. in China, with an average particle size of about 1 μ m. Furthermore, the MG and beta-LAS powders were placed in a grinding bowl and repetitively shaken and stirred at RT in order to obtain a homogeneous mixing of both.

2.2. Manufacture of composites

With the purpose of acquiring composites possessing scheduled behaviors of thermal expansion, the MG powders



Fig. 1 – Characterization of the bonding quality of composites. (a) The diagram of the process for preparing composites with MG and beta-LAS. (b) A picture of MG particles in SEM. (c) A picture of beta-LAS powder in SEM. (d) A photo of the composite prepared by MG and beta-LAS in an equal volume ratio. (e) The SEM morphology of the fractured surface of MG/beta-LAS composites. (f–g) Morphology of polished surfaces of MG/beta-LAS composites in SEM using various magnifications. (h–j)



Fig. 2 — Mechanical properties regulation of MG/beta-LAS composites. (a) The result of XRD tests performed on MG/beta-LAS composites that were fabricated from 0 to 100% beta-LAS by volume proportion. (b) Compressive stress and strain results of MG/beta-LAS composites that were fabricated by various beta-LAS volume proportions. (c) The results of high-resolution CT, which were counterparts for MG/beta-LAS composites fabricated from 20% to 80% MG volume proportion.

exhibiting PTE were homogenously mixed with the additive beta-LAS featuring NTE in a calculated volume ratio and then put into a mold cavity. Next, the mold cavity was vacuumed, and the mixture was subjected to a pre-pressure of 0.8 kN. Once the temperature reached the SLR of the Zr-based MG (~750 K), 10 kN of stress was imposed at a strain rate of 0.1 mm/s and held down for approximately 1 min. Benefiting from the excellent flow and forming ability of MG, the mixture

Result of high-resolution TEM in the MG area, interface area, and beta-LAS area, respectively, from the composites. (k—m) The patterns of diffraction corresponding to the R1, R2, and R3 areas in the high-resolution TEM results. (n) The results of elemental distribution at the interface of this MG/beta-LAS composite. forms a dense solid under pressure, which is then rapidly cooled down to RT.

2.3. Characterization of multi-scale structures

The amorphous and crystalline analysis of the MG and beta-LAS powders, along with the presently fabricated composites, has been performed using copper Ka radiation in X-ray diffraction (XRD; Rigaku MiniFlex600). All these XRD tests were performed using a 5°/min scan speed and 0.02° scan intervals over the range for scan angles 2θ from 20° to 80° . The glass transition temperature (Tg) and crystallization temperature (T_x) of the Zr-based MG particles were measured at a 20 K/min heating rate with differential scanning calorimetry (DSC; PerkinElmer DSC-8000). Moreover, the measurements were performed in an extremely pure argon gas atmosphere. Characteristics of the bonding quality as well as the distribution of elements in this fabricated composite were performed via instrumentation with scanning electron microscopy (SEM; FEI QUANTA FEG 450) in field emission. Composites were first prepared as transmission electron microscopy (TEM) samples at the FEI Scios SEM/FIB dual-beam system and then characterized for atomic structure using TEM with energy dispersive spectroscopy (EDS/TEM; JEM-2100F). Possible various flaws existing inside this composite due to bonding quality were detected by a high-resolution computed laminography scanner (CT, China Sanying Precision Devices, Nano Voxel 3000d). After the samples had been polished until the ends became mutually parallel, they were subjected to CTE and compression properties tests. Testing of the CTE has been performed via a thermodynamic analyzer (TMA; 402 F3, NETZSCH, Germany) in the temperature analysis range of 140-760 K, conducted at a speed of 5 K/min, and filled with high-purity N₂ gas. The sample was a cylinder that measured 5 and 10 mm in diameter and length, respectively. A Zwick electronic multifunctional machine (Z050 TEW) that exhibits a rate of strain of 0.001 s⁻¹ has been utilized to conduct compression tests under RT for cylinders meeting ASTM standards [46]. Where the length and diameter of the cylinders were 7.5 and 5 mm, respectively. The compression stress at 223, 493, and 693 K was measured using a high and low temperature universal mechanical testing machine (UTM5105GD) with a loading rate of 0.06 mm/min.

3. Results and discussion

3.1. Bonding of the NZTE composite

The fabrication of NZTE composites via beta-LAS and MG powder is graphically shown in Fig. 1a, where the prepared NZTE is formed into dense, homogenous cylinders. From this schematic diagram, it can be seen that the whole preparation process was relatively simple. The results of MG as well as beta-LAS powders observed using SEM are displayed, respectively, in Fig. 1b and c. A DSC test of Zr-based MG showed that T_g and T_x were 685 and 765 K, respectively (see Fig. S1). A photo of NZTE composites made from MG and beta-LAS powders with equal volume fractions is shown in Fig. 1d. As seen in the photo, a dense solid has been successfully prepared with MG

and beta-LAS powder. The quality of combination in composites exerts a significant effect on their own mechanical properties [36], so the quality as well as the mechanism of combination were studied. The SEM morphology of the fracture surface for the MG/beta-LAS composite is presented in Fig. 1e. There were extremely uniform distributions of MG (bright phase) and beta-LAS (dark phase), and the MG flow filled the gaps between the beta-LAS particles, which indicates that the MG/beta-LAS composites were well dense. Next, the backscattering mode of SEM has been applied to study the polished surfaces of MG/beta-LAS composites at various magnifications, which are shown in Fig. 1f-g. It was again evidence that MG (bright phase) as well as beta-LAS (dark phase) were evenly distributed inside the composite, while beta-LAS were strongly wrapped around the flowing MG. There is no crack observed at the interface, as well as the presence of obvious wrapping in Fig. 1g. Above these, SEM results demonstrate that excellent bonding between MG and beta-LAS was achieved. A TEM has been employed for characterizing interfaces among MG and beta-LAS of the composites in order to further investigate the composite bonding mechanisms. The high-resolution structures obtained via high-resolution TEM for the combined regions (MG zone, interface zones, and beta-LAS zone) are shown in Fig. 1h-j. There were clear indications for the three zones revealing various atomic structures, with the MG and beta-LAS zones, respectively, being typical of amorphous as well as crystalline structures, while the interface zone was a combination of the two former structures. Additionally, the results of selected area electron diffraction (SAED) for the three marked zones R1, R2, and R3 in the high-resolution TEM results are displayed in Fig. 1k-m. Corresponding to this MG, there was a pure diffraction ring in the zone of R1, thus evidencing that the MG remains amorphous in nature. A combination of crystal dots as well as a halo ring were displayed in the R2 zone on the interface. Moreover, the diffraction results of the R3 zone display a typical crystalline state, which corresponds to beta-LAS.

Fig. 1n illustrates the results obtained using EDS to investigate the elemental distribution of composite interfaces. There were reasons to believe that the mechanical and thermal properties of this composite would certainly benefit from the excellent combination of MG and beta-LAS.

3.2. Mechanical properties

Composites fabricated from beta-LAS containing 20%–80% by volume of XRD test results are shown in Fig. 2a, and results of XRD tests for pure MG as well as beta-LAS are also shown here.

Table 1 – Comparison of the density of composites with different MG addition ratios.			
MG (vol%)	Actual density (g/cm³)	Theoretical density (g/cm³)	Relative density (%)
20	3.0283	3.17	95.53
40	3.5074	3.67	95.56
50	3.7608	3.92	95.94
60	3.9873	4.17	95.62
80	4.4729	4.67	95.78



Fig. 3 — Thermal expansion properties and regulation of MG/beta-LAS composites. (a) Testing of CTE for MG/beta-LAS composites prepared from MG volume rates of 20%—80% as well as pure MG. (b) Investigation of CTE hysteresis in heated and cooled cycles of NZTE composites fabricated by MG at a 50% volume ratio. (c) The compressive stress of composites with a MG volume ratio of 50% at different temperatures. (d) Comparison between the temperature required for the fabrication of different NZTE materials as well as their corresponding range of NTZE temperatures.

Different peaks in these XRD results verify that beta-LAS and Zr-based MG were, respectively, crystalline and amorphous. There were two kinds of peaks assembled in the XRD results for the presently fabricated composites, and they exhibit the trend that the amorphous as well as crystalline peaks, respectively, increase and decrease due to the lowering beta-LAS ratio. Materials that apply to practical engineering normally require certain mechanical capabilities [5]. Therefore, the compressive stress and strain tests were performed on MG/beta-LAS composites that were fabricated from various volume ratios of beta-LAS, as shown in Fig. 2b. Benefiting from the MG strengthening, the composites present a superior compressive stress. As the volume ratio of beta-LAS decreases or the volume ratio of Zr-based MG increases, there is a clear trend towards increasing compressive stress for the composites. The compressive stresses of the composites with a 20%, 40%, 50%, 60%, and 80% volume ratio of beta-LAS were, respectively, 673, 500, 436, 320, and 191 MPa. These results suggest that the mechanical properties of the composite can be regulated to meet various situations.

Those composites were scanned using high-resolution CT in order to investigate internal uniformity as well as various defects that may be present inside the composites. The results of intermediate cross-sectional scans for the composites that were fabricated from 20%, 40%, 50%, 60%, and 80% MG by volume ratio are shown in Fig. 2c. All of the MG (blue zone) as well as beta-LAS (white zone) were evenly distributed inside the composites, where no visible cracks exist. Subsequently, the actual densities of MG, beta-LAS, and composites were measured based on the theory of the Archimedes drainage method. Each specimen's actual density can be calculated based on the following equation:

$$\rho_{\text{actual}} = \left(\omega_1 \times \rho_1\right) / \left(\omega_1 - \omega_2\right) \tag{1}$$

Within equation (1) above, at chamber temperature, distilled aqueous density was replaced with ρ_1 , and the measured weight of the subject under air as well as distilled aqueous conditions was replaced with ω_1 and ω_2 accordingly. After the MG and beta-LAS were tested, the actual densities were 5.17 and 2.67 g/cm³, respectively. The following formula is applied to calculate the theoretical density of the composites:

$$\rho_{\text{theoretical}} = \sum_{x=1}^{n} v_x \rho_x \tag{2}$$

The v_x and ρ_x in Eq. (2), respectively, mean the content of the volume fraction and density for various admixtures among the composites. Composites' actual as well as theoretical densities have been calculated from Eqs. (1) and (2), whose results are displayed in the following Table 1.



Fig. 4 – Interfacial bonding morphology for the MG/beta-LAS compound after thermal cycling. (a–c) The SEM morphology at different magnifications for MG/beta-LAS composites after 50, 80, and 110 thermal cycles. (d) Schematic diagram of the MG/ beta-LAS composites after 50, 80, and 110 thermal cycles.

Obviously, there was almost consistency between the actual and theoretical densities in the composite, and the minimum of the relative density exceeds 95.5%. All the above results demonstrate an effective approach to fabricating compact solids as well as modulating the properties of composites by utilizing the excellent properties of MG.

3.3. Composites with near-zero thermal expansion

The composites possessing NZTE properties were successfully fabricated according to the mentioned strategy. Linear CTE was -6.1 ppm/K for beta-LAS, which has been chosen to be the swelling inhibitor in the fabrication of NZTE composites, where the mean particle size was 1 μ m. The MG/beta-LAS composites that contained MG at 20, 40, 50, 60, and 80% of the volume ratio had been CTE analyzed, as indicated in Fig. 3a. According to those CTE results, there was a marked decline in the CTE of the composites along with a lower ratio of MG content. Equations for calculating the linear CTE of a material are presented below [4]:

$$\alpha = \frac{\Delta L}{L_0 \Delta T} \tag{3}$$

where L_0 , ΔL , and ΔT from Eq. (3), respectively, mean the initial length, elongation, and variation of temperatures among the samples. When the linear CTE in absolute value is smaller than 2 ppm/K, it is known as the NZTE property. After calculation utilizing Eq. (3), it was found that the linear CTE for

composites with MG volume ratios of 20%, 40%, and 50% was 0.221, 0.693, and 1.587 ppm/K in a very extensive range of temperatures (150–700 K), respectively. When 60 vol% of MG was added in the range of temperatures from 150 to 523 K, the linear CTE of the composite was 1.94 ppm/K. But the curve had a very steep trend when 80 vol% MG was added, which was not NZTE. The MG in the range of temperatures from 150 to 700 K exhibits a linear CTE of 8.94 ppm/K. Two interesting things are the following: 1. The linear CTE of the composites fabricated by MG with a 40% volume ratio within 150–573 K was 0.247 ppm/K 2. The linear CTE of the composites prepared by the MG with a 50% volume ratio within 283–483 K was 0.461 ppm/K. Briefly, NZTE composites possessing an extremely wide range of temperatures have been fabricated successfully.

Because most NZTE materials suffer from hysteresis in thermal expansion properties and poor overall mechanical properties due to undesirable microstructure or weak interfacial bonding [14], the MG/beta-LAS composites prepared in equal volume ratios were chosen for testing the hysteresis in thermal expansion properties. Both the red and blue lines of Fig. 3b illustrate the results of CTE testing during heating and cooling, respectively, for this composite. It can be found that the trends of the four hot and cold cycles performed within the 150–700 K range of test temperatures as well as at a 5 K/ min rate of heating were nearly identical, revealing an extremely slight hysteresis phenomenon. As shown in Fig. 3c, the compressive strengths of this composite were 427, 431,



Fig. 5 – Various NZTE components and corresponding SEM images. (a–f) Gear, gasket without round hole, seal ring, gasket, micron-level matrix, and cylindrical pins of different sizes fabricated by the present NZTE composite with its corresponding SEM morphology. (g) The group photo of various components fabricated by the present NZTE composites.

and 418 MPa at 223, 493, and 693 K, respectively. There were some differences in the compressive strength for varying temperatures, as well as a lowering of the compressive strength at high and low temperatures compared to RT (293 K), which were consistent with the traditional results. Significantly, the amount of change in compressive stress at varying temperatures was closely related to the CTE. The CTE for MG volume ratio 50% composites was 0.265, 1.557, and 1.958 ppm/ K, respectively, during 293-473 K, 293-673 K, and 223-293 K. The compressive stresses of this composite at 293, 473, and 673 K were, respectively, decreased by about 5, 18, and 9 MPa compared to RT. With the increase in temperature, the compressive stress would be reduced more. Combining the effects of temperature and CTE, it is normal for the compressive stress at 223 K to be slightly higher than at 697 K. Overall, it was found that smaller CTE showed a more obvious effect on suppressing the variation of compression strength with temperature; hence, the mechanical properties of NZTE composites in this work were relatively stable at different temperatures.

Summaries of fabrication temperatures as well as the temperature range for NZTE materials from references (available in Table S1) are shown in Fig. 3d. As can be seen, the present composites exhibit significant advantages compared to most NZTE materials with respect to preparation temperature as well as temperature range. As a result, the strategy proposed in this work for the fabrication of NZTE composites was universal as well as efficient. This strategy not only reduces costs but also stimulates the fabrication of high-performance NZTE materials from hard searching towards manually designable.

The thermal shock resistance under thermal cycling for NZTE composite in practical field applications has significant value. To check how many thermal cycles the NZTE composites fabricated from MG and beta-LAS at equal volume ratios can sustain without degradation, they were placed inside a vacuum stove and subjected to 50, 80, and 110 cycles of heating and cooling, respectively. After undergoing heated and cooled cycles, as shown in Fig. 4a–c, the results of polished morphology for this NZTE composite were studied at various magnifications by applying backscattering mode.

It can be found that microcracks were observed inside the MG/beta-LAS composite after 50 cycles. In addition, cracks appeared in the composite after 80 cycles, and apparent fractures occurred after 110 cycles. Fig. 4d shows a schematic diagram of the MG/beta-LAS composite after 50, 80, and 110 thermal cycles. It can be seen more clearly that the internal cracks become gradually larger and increase as the number of thermal cycles increases; moreover, the cracks appeared only at the interfaces of the two materials as well as in the beta-LAS region. According to those results, one can conclude that the MG/beta-LAS composite with a 50% MG volume ratio exhibits superior thermal shock resistance and can withstand thermal cycling tests of not less than 80 times.

Materials that can be applied to engineering require certain shape flexibility and processing capabilities; thus, this work utilizes the presently obtained NZTE composites to fabricate various components. Fig. 5a shows the gear fabricated from the present NZTE composites and the gear with the number of teeth 33, the normal modulus 0.2 mm, and the top circle diameter 6.98 mm. The partial magnification of the gear in the SEM of the backscattering mode showed a very clear tooth profile and a uniform distribution of the two-phase material. To further verify the excellent shape flexibility of the present NZTE composites, gaskets of 8 mm in diameter with structures around and without circular holes in the middle were prepared, as shown in Fig. 5b. The physical picture of this nonround hole gasket as well as the SEM morphology once again demonstrate the excellent shape flexibility of the present NZTE composite. In addition, sealing rings and gaskets were successfully prepared by drilling and wire-cutting processes in cylinders of 5 and 8 mm of diameter fabricated from this NZTE composite, as shown in Fig. 5c and d. The outer diameter of the seal ring was 5 mm, and the diameter of the middle hole was 2 mm. The outer diameter of the gasket was 8 mm, the diameter of the middle hole was 3 mm, and there was a structure around it. Fig. 5c-d verify that the present NZTE composites possess certain processing capabilities. Fig. 5e shows the micron-level matrix prepared from the present NZTE composites, and this result indicates that the composites possess certain micron-level shape flexibility. Fig. 5f shows different sizes of cylindrical pins prepared from the present NZTE composite. The different diameters and heights fully demonstrate the adjustability of the dimensions of this composite molding. The components prepared from the present NZTE composites in this work are summarized together in Fig. 5g. Various NZTE components were fabricated to demonstrate that the NZTE composites prepared from MG/beta-LAS composites possess excellent shape flexibility and processing capabilities with great promise for engineering applications.

4. Conclusion

Overall, this study devised a universal and effective strategy to fabricate metallic glass matrix composites that exhibit high compressive strength and NZTE in a very wide temperature region while achieving regulation towards CTE and compressive stress. Due to the excellent bonding and forming abilities of MG in SLR, the relative density of the composite prepared by beta-LAS and MG exceeds 95.5%. Benefiting from this strategy, the NZTE properties were acquired in the temperature region from 150 to 700 K ($\Delta T = 550$ K) by adding MG with 20, 40, and 50 vol% and exhibited linear CTE of 0.221, 0.693, and 1.587 ppm/K, respectively. These three ratios of NZTE composites exhibit respective compressive stresses of 191, 320, and 436 MPa. Regulation of CTE and compressive stress was achieved through changing the volume ratio content of MG and beta-LAS, which showed the prospect that the preparation of well-performing NZTE composites can be transformed from a laborious search to a customizable process. In addition, the thermal shock resistance results showed that the composite can withstand thermal cycling tests of not less than 80 times, and the various NZTE components fabricated demonstrate the flexibility of the proposed strategy. As a result, this study provided well-integrated NZTE composites that will exhibit significant prospects for satellite communications, microelectronics, and precision instrumentation applications.

Author contribution

Shike Huang: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. Fei Sun: Investigation, Methodology, Project administration, Writing – review & editing. Wenqing Ruan: Supervision. Shuai Ren: Supervision. Zhenxuan Zhang: Supervision. Xiong Liang: Supervision. Jiang Ma: Investigation, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The work was supported by the Key Basic and Applied Research Program of Guangdong Province, China (Grant Nr. 2019B030302010), the NSF of China (Grant Nr. 52122105, 51871157, 51971150), the National Key Research and Development Program of China (Grant No. 2018YFA0703604). The authors also thank the assistance on microscope observation received from the Electron Microscope Center of Shenzhen University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmrt.2023.06.097.

REFERENCES

- [1] Jiang XX, Molokeev MS, Gong PF, Yang Y, Wang W, Wang SH, et al. Near-zero thermal expansion and high ultraviolet transparency in a borate crystal of Zn₄B₆O₁₃. Adv Mater 2016;28(36):7936–40.
- [2] Sleight A. Materials science zero-expansion plan. Nature 2003;425(6959):674-6.
- [3] Chen J, Hu L, Deng J, Xing X. Negative thermal expansion in functional materials: controllable thermal expansion by chemical modifications. Chem Soc Rev 2015;44(11):3522–67.
- [4] Roy R, Agrawal DK, McKinstry HA. Very low thermal expansion coefficient materials. Annu Rev Mater Sci 1989;19(1):59–81.
- [5] Hartmann P, Jedamzik R, Carré A, Krieg J, Westerhoff T. Glass ceramic zerodur®: even closer to zero thermal expansion: a review, part 1. J Astronomical Telesc Instrum Syst 2021;7(2).
- [6] Yang C, Li J, Wang X, Yang D, Shi H, Meng S, et al. ZrW₂O₈/ ZrO₂ composites with low/near-zero coefficients of thermal expansion fabricated at ultralow temperature: an integration of hydrothermal assembly and a cold sintering process. ACS Appl Mater Interfaces 2021;13(33):39738–47.
- [7] Wang J, Zhang Y, Di KC, Chen M, Duan JF, Kong J, et al. Localization of the Chang'e-5 lander using radio-tracking and image-based methods. Remote Sens 2021;13(4).

- [8] Marinkovic BA, Pontón PI, Romao CP, Moreira T, White MA. Negative and Near-zero thermal expansion in A₂M₃O₁₂ and related ceramic families: a review. Front Magn Mater 2021;8.
- [9] Ding L, Wang C, Na Y, Chu L, Yan J. Preparation and near zero thermal expansion property of Mn₃Cu_{0.5}A_{0.5}N (A=Ni, Sn)/Cu composites. Scr Mater 2011;65(8):687–90.
- [10] Yamamoto N, Gdoutos E, Toda R, White V, Manohara H, Daraio C. Thin films with ultra-low thermal expansion. Adv Mater 2014;26(19):3076–80.
- [11] Kainuma R, Wang JJ, Omori T, Sutou Y, Ishida K. Invar-type effect induced by cold-rolling deformation in shape memory alloys. Appl Phys Lett 2002;80(23):4348–50.
- [12] Shiga M. Invar alloys. Curr Opin Solid State Mater Sci 1996;1(3):340-8.
- [13] Yan X, Miao J, Liu J, Wu X, Zou H, Sha D, et al. Zero thermal expansion, electrical conductivity and hardness of Mn₃Zn_{0.5}Sn_{0.5}N/Cu composites. J Alloys Compd 2016;677:52–6.
- [14] Yu C, Lin K, Jiang S, Cao Y, Li W, Wang Y, et al. Plastic and low-cost axial zero thermal expansion alloy by a natural dual-phase composite. Nat Commun 2021;12(1):4701.
- [15] Takezawa A, Kobashi M. Design methodology for porous composites with tunable thermal expansion produced by multi-material topology optimization and additive manufacturing. Compos B Eng 2017;131:21–9.
- [16] Pang XL, Song YZ, Shi NK, Xu M, Zhou C, Chen J. Design of zero thermal expansion and high thermal conductivity in machinable xLFCS/Cu metal matrix composites. Compos B Eng 2022:238.
- [17] Takenaka K. Negative thermal expansion materials: technological key for control of thermal expansion. Sci Technol Adv Mater 2012;13(1).
- [18] Xue ZW, Wang LD, Liu Z, Fei WD. Effect of interfacial state on thermal expansion behaviors of β -LiAlSiO₄ particulate-reinforced Cu composites. Scr Mater 2010;62(11):867–70.
- [19] Holzer H, Dunand DC. Phase transformation and thermal expansion of Cu/ZrW_2O_8 metal matrix composites. J Mater Res 1999;14(3):780–9.
- [20] Mary TA, Evans JSO, Vogt T, Sleight AW. Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW₂O₈. Science 1996;272(5258):90–2.
- [21] Peng Z, Sun YZ, Peng LM. Hydrothermal synthesis of ZrW₂O₈ nanorods and its application in ZrW₂O₈/Cu composites with controllable thermal expansion coefficients. Mater Des 2014;54:989–94.
- [22] Wu Y, Wang M, Chen Z, Ma N, Wang H. The effect of phase transformation on the thermal expansion property in Al/ ZrW₂O₈ composites. J Mater Sci 2012;48(7):2928–33.
- [23] Zhou C, Zhang Q, Liu S, Zhou T, Jokisaari JR, Wu G. Microstructure and thermal expansion analysis of porous ZrW₂O₈/Al composite. J Alloys Compd 2016;670:182–7.
- [24] Zhou C, Zhang Q, Liu S, Zhou T, Jokisaari JR, Wu G. Near-zero thermal expansion of ZrW₂O₈/Al–Si composites with three dimensional interpenetrating network structure. Compos B Eng 2021:211.
- [26] Tani J, Takahashi M, Kido H. Fabrication and thermal expansion properties of ZrW₂O₈/Zr₂WP₂O₁₂ composites. J Eur Ceram Soc 2010;30(6):1483–8.
- [27] Hao X, Zhou H, Mu B, Chen L, Guo Q, Yi X, et al. Effects of fiber geometry and orientation distribution on the anisotropy of mechanical properties, creep behavior, and thermal expansion of natural fiber/HDPE composites. Compos B Eng 2020:185.
- [28] Lee D, Song YS. Modeling the effects of elastic modulus and thermal expansion coefficient on the shrinkage of glass fiber reinforced composites. Compos B Eng 2018;146:98–105.

- [29] Ding L, Wang C, Na Y, Chu L, Yan J. Preparation and near zero thermal expansion property of Mn₃Cu_{0.5}A_{0.5}N (A=Ni, Sn)/Cu composites. Scr Mater 2011;65(8):687–90.
- [30] Hu L, Chen J, Fan L, Ren Y, Rong Y, Pan Z, et al. Zero thermal expansion and ferromagnetism in cubic $Sc_{(1-x)}M_{(x)}F_3$ (M = Ga, Fe) over a wide temperature range. J Am Chem Soc 2014;136(39):13566–9.
- [31] Hu L, Chen J, Xu J, Wang N, Han F, Ren Y, et al. Atomic linkage flexibility tuned isotropic negative, zero, and positive thermal expansion in MZrF6 (M = Ca, Mn, Fe, Co, Ni, and Zn). J Am Chem Soc 2016;138(44):14530–3.
- [32] Romao CP, Perras FA, Werner-Zwanziger U, Lussier JA, Miller KJ, Calahoo CM, et al. Zero thermal expansion in ZrMgMo₃O₁₂: NMR crystallography reveals origins of thermoelastic properties. Chem Mater 2015;27(7):2633–46.
- [33] Serebrennikov DA, Bykov AA, Trigub AL, Kolyshkin NA, Freydman AL, Aborkin AV, et al. Near zero thermal expansion in metal matrix composites based on intermediate valence systems: Al/SmB₆. Results Phys 2021:21.
- [34] Yan J, Sun Y, Wang C, Chu L, Shi Z, Deng S, et al. Study of structure of Mn₃Cu_{0.5}Ge_{0.5}N/Cu composite with nearly zero thermal expansion behavior around room temperature. Scr Mater 2014;84–85:19–22.
- [35] Greer AL. Metallic glasses. Science 1995;267(5206):1947-53.
- [36] Sun F, Lin H, Fu J, Li Z, Luo F, Wang B, et al. Metallic glass based composites with precise tunable thermal expansion. Appl Mater Today 2022;29:101565.

- [37] Maeda M, Takahashi Y, Fukuhara M, Wang X, Inoue A. Ultrasonic bonding of Zr₅₅Cu₃₀Ni₅Al₁₀ metallic glass. Mater Sci Eng B 2008;148(1–3):141–4.
- $\label{eq:starses} \begin{array}{l} \mbox{[38]} \\ \mbox{Haruyama O, Nakayama Y, Wada R, Tokunaga H, Okada J, \\ \mbox{Ishikawa T, et al. Volume and enthalpy relaxation in $Zr_{55}Cu_{30}$ \\ \mbox{Ni}_5Al_{10}$ bulk metallic glass. Acta Mater 2010;58(5):1829-36. \\ \end{array}$
- [39] Li N, Chen Y, Jiang MQ, Li DJ, He JJ, Wu Y, et al. A thermoplastic forming map of a Zr-based bulk metallic glass. Acta Mater 2013;61(6):1921–31.
- [40] Li H, Li Z, Yang J, Ke HB, Sun B, Yuan CC, et al. Interface design enabled manufacture of giant metallic glasses. Sci China Mater 2021;64(4):964–72.
- [41] Kumar G, Tang HX, Schroers J. Nanomoulding with amorphous metals. Nature 2009;457(7231):868–72.
- [42] Ma J, Yang C, Liu XD, Shang BS, He QF, Li FC, et al. Fast surface dynamics enabled cold joining of metallic glasses. Sci Adv 2019;5(11).
- [43] Schroers J, Pham Q, Peker A, Paton N, Curtis RV. Blow molding of bulk metallic glass. Scr Mater 2007;57(4):341–4.
- [44] Duan G, Wiest A, Lind ML, Li J, Rhim WK, Johnson WL. Bulk metallic glass with benchmark thermoplastic processability. Adv Mater 2007;19(23):4272–5.
- [45] Fu J, Yang J, Wu K, Lin H, Wen W, Ruan W, et al. Metallic glue for designing composite materials with tailorable properties. Mater Horiz 2021;8(6):1690–9.
- [46] E. ASTM. Standard test methods of compression testing of metallic materials at room temperature. ASTM International; 2000. p. 98–105.