Article

Investigation of Thermophysical Properties of Zr-Based Metallic Glass-Polymer Composite

Adit Sharma ^{*} , Mikhail Zadorozhnyy, Andrey Stepashkin, Aksar Kvaratskheliya, Artem Korol, Dmitri Moskovskikh , Sergey Kaloshkin and Vladislav Zadorozhnyy ^{*}

Centre of Composite Materials, National University of Science and Technology “MISIS”, Leninsky Prospekt, 4, 119049 Moscow, Russia; zadorozhnyy.mihail@gmail.com (M.Z.); a.stepashkin@yandex.ru (A.S.); aaaaskar123@gmail.com (A.K.); artemkorol1998@gmail.com (A.K.); mos@misis.ru (D.M.); Kaloshkin@misis.ru (S.K.)

^{*} Correspondence: adit15@yandex.com (A.S.); vuz@misis.ru (V.Z.)

Abstract: Composites based on $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ metallic glass (MG) and polytetrafluoroethylene (PTFE) were prepared by ball milling. Different composites (30/70, 50/50 and 70/30) were produced. Samples for dynamic mechanical analysis and laser flash analysis were fabricated in the supercooled region of the metallic glass and viscous region of the polymer. Spark plasma sintering (SPS) was performed at the supercooled region for the metallic glass powder. Characteristics such as thermal, mechanical, and structural properties were studied. A formation of the Zr_2Cu and Zr_2Ni intermetallic was found in the metallic glass after SPS. A formation of the nanocrystalline Zr_2Cu was found in composite samples. Dynamical mechanical analysis (DMA) was used to study the mechanical behavior of the material. It was concluded that the 70/30-MG/PTFE composite sample had better thermal conductivity than the other composite samples. The thermal conductivity of the metallic glass was the highest among the samples and it increased with the MG content in composites.

Keywords: metallic glass; polymer; composite; ball milling; X-ray diffraction; thermal properties; dynamic mechanical analysis

Citation: Sharma, A.; Zadorozhnyy, M.; Stepashkin, A.; Kvaratskheliya, A.; Korol, A.; Moskovskikh, D.; Kaloshkin, S.; Zadorozhnyy, V. Investigation of Thermophysical Properties of Zr-Based Metallic Glass-Polymer Composite. *Metals* **2021**, *11*, 1412. <https://doi.org/10.3390/met11091412>

Academic Editors: Tadeusz Kulik and Jordi Sort Viñas

Received: 2 August 2021

Accepted: 3 September 2021

Published: 7 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Metallic glass (MG) has attracted attention worldwide due to its excellent properties. It is known for its excellent mechanical, electrical, and magnetic properties [1] and is mainly produced by rapid solidification techniques [2]. Due to its amorphous structure, it does not have crystalline defects and grain boundaries compared to crystalline materials [3]. This leads to better properties, such as high mechanical strength, wear and corrosion resistance [4]. The limitations of metallic glass are its brittle nature and the formation of shear bands during plastic deformation [5]. This limits its potential application. Polymers are ductile, with low strength and low density [6]. Composite materials have shown considerable improvement in mechanical, optical, electrical, and magnetic properties [7]. The combination of metallic glass and polymer can produce a lightweight composite with enhanced thermal and mechanical properties. Metallic glass production is cheap and can be produced by sputtering, melt-spinning techniques, powder metallurgy, liquid quenching, magnetron sputtering and pulsed laser quenching [8]. Zr-Cu-based metallic glass is inexpensive and has attracted attention due to its thermal stability, as well as its mechanical and corrosion properties [9]. Tang [10] et al. investigated the mechanical properties of Zr-based metallic glass and found that it has good plasticity with plastic strain. $Zr_{40}Ti_{35}Ni_{14}Nb_{11}$ metallic glass can be used as bioimplant material [11]. Zr-Al-Fe-Cu metallic glass is known for its corrosive properties and can be used as a stent [12]. The addition of aluminum in Zr-Cu improves the mechanical properties and thermal stability of metallic glass [13–15]. Nickel increases the corrosion resistance, glass transition temperature and mechanical properties [16–19]. Zr-Cu-Ni-Al metallic glass is used in the

manufacturing of nanowires and electronic and biomedical instruments [20–22]. Zr-Cu-Ni-Al metallic glass has a high glass-forming ability [23]. Zr-based metallic glass showed antibacterial characteristics [24].

Polytetrafluoroethylene (PTFE) is thermoplastic in nature. PTFE is inexpensive and shows mechanical endurance and resistance to chemicals [25]. PTFE composite [26] demonstrates enhanced mechanical and tribological properties. PTFE is used in bioimplants due to its inert traits [27]. PTFE composites have high thermal conductivity [28]. The increase in the molar fraction concentration of the PA6 polymer in PTFE blends increases the flexural properties and improves adhesion in the composite [29]. PTFE-Al-W composite showed an increase in ultimate compressive strength regardless of high porosity [30]. Ag-Au/PTFE composite has antibacterial properties [31]. Due to its properties, PTFE is an ideal candidate for the preparation of composites with Zr-based metallic glass.

Cu-Zr metallic glass/polyisoprene nanolaminates [32] show an increase in the plastic flow of composites. The composite can be used in nanodevices and corrosion resistance applications. $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ metallic glass/polyphenylene sulfide (PPS) composite shows good bonding between the composite [33]. $\text{Fe}_{64}\text{Co}_{17}\text{Si}_7\text{B}_{12}$ /Polyvinylidene fluoride [34] (PVDF) composite can be used in ultra-low-power applications such as miniaturized electronic devices. Zr-based metallic glass thin film/polyacrylonitrile (PAN) composite membranes are more permeable for N_2 than O_2 and CO_2 [35]. Previously, a successful dual-phase metallic glass composite was prepared by ball milling [36] and coextrusion [37]. Hence, it is possible to create a composite [38] based on metallic glass and polymer by ball milling and coextrusion. The temperature of the process is generally in the supercooled region [39] (between the glass transition temperature T_g and crystallization temperature T_x).

In our previous studies, composites were produced by ball milling and coextrusion. $\text{Mg}_{67.5}\text{Ca}_5\text{Zn}_{27.5}$ /High Density Poly Ethylene (HDPE) [40] composite was prepared by co-extrusion and compression in the supercooled region. The composite showed good adhesive properties. $\text{Cu}_{54}\text{Pd}_{28}\text{P}_{18}$ /PTFE composite [41] was produced by ball milling and subsequent spark plasma sintering (SPS). The SPS temperature was near the supercooled temperature of the composite. The composite showed better thermal conductivity as compared to the PTFE. $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$ /(Polyethylene terephthalate) PET composite [42] was developed by ball milling and spark plasma sintering. Additionally, the composite showed good thermal properties as compared to $\text{Mg}_{67.5}\text{Ca}_5\text{Zn}_{27.5}$ and $\text{Cu}_{54}\text{Pd}_{28}\text{P}_{18}$ metallic glasses. In another study, $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$ /Polycaprolactone (PCL) [43] composite was produced by ball milling and subsequent co-extrusion. The co-extrusion temperature was near the supercooled temperature of the metallic glass. The composite properties were investigated for mechanical and thermal properties. In vivo studies showed that the composite is biocompatible.

In the present study, a composite ($\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ /PTFE) was produced by ball milling. Metallic glass is known for its mechanical properties but lacks ductility. Although the polymer has low strength, it has plasticity. The main criteria of this work are to produce a composite with good mechanical properties. Sintering of the composite was performed at the supercooled region of the metallic glass and liquid state of the polymer. Thus, in our mind, this is the ideal condition to prepare enhanced composites with enhanced properties.

2. Material and Methods

Ingots of $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ alloy were fabricated by induction melting (Diavac Ltd., Yachiyo, Chiba, Japan) in an argon atmosphere by arc melting from mixtures of pure Zr, Cu, Ni, and Al (purity of each element used was $\approx 99.9\%$). Metallic glass ribbons were prepared by single copper roller melt spinning (under an argon atmosphere). The thickness of the ribbons was 20–30 μm . The width of the ribbons was 4.7–4.9 mm. The average size of the polytetrafluoroethylene powder (PTFE-F4) was about 10–15 μm .

Ball milling of the samples was performed using a planetary mill (Fritsch Pulverisette 5, Berlin, Germany) with a rotation speed of 300 rotations per minute (rpm) under an argon atmosphere. The total duration of ball milling for the metallic glass was 30 min. The

average size of the MG particles was about 10 μm . The powdered metallic glass was added to the polymer for the ball milling process. Different composite samples of metallic glass/polymer ratios (mass.%) of 30/70, 50/50 and 70/30 were prepared. The mixing time for the composite samples was 30 min, each under a rotation speed of 300 rpm.

For the spark plasma sintering (SPS) measurement, the metallic glass powder was inserted inside graphite die with an inner diameter of 12.7 mm, an outer diameter of 30 mm, and a height of 30 mm. The sample was wrapped in a 0.2 mm thick graphite sheet. The sheet was used to prevent the sample from die contact. The powder was sintered using SPS [44] (Labox 650, Sinter Land inc, Nagaoka, Niigata Prefecture, Japan). The heating rate was 50 $^{\circ}\text{C}/\text{min}$, with a maximum temperature of 400 $^{\circ}\text{C}$, under a pressure of 50 MPa and 50 min duration.

X-ray diffraction (XRD) (Research and production enterprise “Bourestnik”, Saint Petersburg, Russian Federation) on a DRON Diffractometer, under $\text{CoK}\alpha$ radiation (2θ angles: 10 to 120 $^{\circ}$, step: 0.1 $^{\circ}$, exposition time per step: 5s, beam size: 6–8 mm) was used to determine the phase and structural composition of samples. The accuracy of the phase composition was $\pm 5\%$. The kinematic standard method and annealed powder use a standard to determine the percentage of amorphous phase [45].

A differential scanning calorimeter (DSC) (NETZSCH DSC 204 F1) (Netzsch Erich Netzsch GmbH & Co. Selb, Upper Franconia, Bavaria, Germany) was used for thermal analysis. The heating rate was 10 $^{\circ}\text{C}/\text{min}$ under an argon atmosphere. The sample mass was between 10 and 15 mg. The maximum temperature of the DSC was 600 $^{\circ}\text{C}$ to study the supercooled region and crystallization and 320 $^{\circ}\text{C}$ for the measurement of heat capacity of the samples. It was used to determine the glass transition temperature (T_g) and the onset of the crystallization temperature (T_x) using a computer application.

A dynamic mechanical analyzer model Q800 (TA Instruments, New Castle, DE, USA) was used to measure the viscoelastic properties as a function of temperature. For dynamic mechanical analysis (DMA) [46], a dual cantilever (bending) was used for composite samples and PTFE and a tensile clamp for the metallic glass ribbon. The dimensions for the specimens were a length of 30 mm, a width of 5.05 mm, and a thickness of 1.30 mm ($30 \times 5.05 \times 1.30$). The temperature for the samples was 400 $^{\circ}\text{C}$ at a heating rate of 2 K/min. The samples were examined at 0.1, 1 and 10 Hz with a dynamic strain of 0.1%.

Loss factor ($\tan \delta$) was used to calculate the internal friction and damping of the samples, which was calculated using the following equation:

$$\tan \delta = E''/E' \quad (1)$$

where E'' is loss modulus, and E' is storage modulus. DMA was used to study the storage modulus (E') and loss factor ($\tan \delta$) under heating.

Thermal diffusivity of the samples was studied by Netzsch LFA 447 NanoFlash (Netzsch Erich Netzsch GmbH & Co., Selb, Upper Franconia, Bavaria, Germany). The temperature range was between 25 and 300 $^{\circ}\text{C}$.

The calculation for thermal conductivity was performed using the following equation:

$$\lambda = \alpha C_p \rho \quad (2)$$

where α is the thermal diffusivity (mm^2/s), C_p is the specific heat capacity J/g·K, and ρ is the sample density (g/cm^3).

SPS was used to produce a metallic glass sample in a bulk state. The samples for thermal diffusivity were obtained in the form of a circular disk 12.7 mm in diameter. A shop press was used to prepare the similar circular disk from composite powders, and subsequent sintering was performed in a vacuum furnace (PT 200) at 400 $^{\circ}\text{C}$ for 4 h and air-cooled for 1 h. The densities of the samples were measured by the hydrostatic weighing method using the AND GR-202 analytical balance and by using the AND AD-1653 set for density determination in ethanol.

A scanning electron microscope SEM, (Hitachi TM-1000, Tokyo, Japan) was used to study the microstructure of the samples at 15 kV in backscattered mode.

3. Results

3.1. X-ray Diffraction Analysis (XRD)

The broad diffraction pattern (Figure 1a) of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass shows its amorphous nature. Amorphous broad halo diffraction can be seen at $2\theta \approx 38\text{--}50^\circ$ in the XRD pattern. After ball milling (Figure 1b), the metallic glass stayed amorphous. The XRD pattern of the metallic glass after SPS (Figure 1c) shows that the metallic glass was semicrystalline. After SPS, there was a formation of crystalline Zr_2Ni and Zr_2Cu phases in the metallic glass [47]. As compared to our previous results, it should be concluded that the intermetallic phases were formed during the SPS procedure. PTFE (Figure 1d) shows a crystalline nature with the most intensive peak at $2\theta = 21^\circ$. The composite materials 30/70 (Figure 1e), 50/50 (Figure 1f) and 70/30 (Figure 1g) show crystalline peaks similar to PTFE. The broad spectrum from the peak at $2\theta \approx 38\text{--}50^\circ$ shows the amorphous nature of the 30/70, 50/50 and 70/30 composite samples, with a small nanocrystalline Zr_2Cu phase (no more than 5%).

Figure 1. XRD pattern of the (a) $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass, (b) $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass after ball milling at 300 rpm, (c) metallic glass after SPS, (d) PTFE polymer, (e) 30/70 composite (f) 50/50 composite, and (g) 70/30 composite.

3.2. Differential Scanning Calorimetry (DSC)

The DSC thermogram of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass (Figure 2a) shows that T_g is 374°C and T_x is 461°C . The $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass has a large supercooled region of 87°C . This is in good agreement with the work of Abrosimova et al. [48]. The heating rate for the metallic glass sample is $10^\circ\text{C}/\text{min}$. The melting temperature of the PTFE is 341°C (Figure 2b). The composite samples have a melting point near the PTFE. The

criteria for choosing the polymer were its physical properties and its melting temperature near the supercooled region of the metallic glass. This criterion was also used in our previous works [41–43]. The composites have a melting temperature of 346 °C for 30/70, 347 °C for 50/50 and 348 °C for 70/30 (Figure 2b) composites.

Figure 2. DSC analysis of (a) $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass, (b) PTFE, and 30/70, 50/50 and 70/30 composites.

3.3. Dynamic Mechanical Analysis

DMA was used to study the atomic ability [49] of the metallic glass, PTFE and their composites. Atomic mobility is decreased by the structural relaxation due to a decrease in the defect concentration. The loss factor ($\tan \delta$) increases with an increase in defect mobility. The change in the atomic mobility influences the structural relaxation and internal friction that caused α and β relaxation in the composite and PTFE samples. For the metallic glass (Figure 3a), the storage modulus is maximum at 250 °C at 0.1 Hz, 270 °C at 1 Hz and 301 °C at 10 Hz. The loss factor ($\tan \delta$) increases with an increase in temperature. The maximum value for the metallic glass is $31,691 \pm 317$ MPa at 0.1 Hz, $31,194 \pm 312$ MPa at 1 Hz and $31,428 \pm 314$ MPa at 10 Hz. The 70/30 composite (Figure 3e) has the highest storage modulus compared to the 30/70 and 50/50 composites (Figure 3c,d). PTFE has the lowest storage modulus among the samples (Figure 3b).

3.4. Laser Flash Analysis (LFA)

The thermal conductivity of the metallic glass (Figure 4) increases with an increase in temperature. It has the highest thermal conductivity (Table 1) compared to other samples. The 70/30 composite (Figure 4) has relatively higher thermal conductivity than the 50/50 and 30/70 composites. PTFE (Figure 4) has the lowest thermal conductivity among the samples.

Figure 3. DMA analysis of (a) metallic glass, (b) PTFE, (c) 30/70 composite, (d) 50/50 composite and (e) 70/30 composite.

Figure 4. Thermal conductivity of metallic glass 50/50 composite, 70/30 composite, Pure PTFE and 30/70 composite.

Table 1. Thermal properties of the samples.

Temperature Analysis, °C	25	50	100	150	200	250	300
PTFE							
Thermal diffusivity, mm ² /s	0.138 ± 0.03	0.147 ± 0.007	0.141 ± 0.001	0.134 ± 0.001	0.125 ± 0.001	0.115 ± 0.003	0.104 ± 0.007
Thermal conductivity, W·m ⁻¹ ·K ⁻¹	0.090 ± 0.01	0.099 ± 0.01	0.103 ± 0.02	0.103 ± 0.01	0.0101 ± 0.01	0.099 ± 0.02	0.098 ± 0.01
Heat capacity, J/(g·K)	0.411 ± 0.02	0.421 ± 0.02	0.459 ± 0.02	0.483 ± 0.02	0.509 ± 0.02	0.540 ± 0.02	0.589 ± 0.02
Sample density, g/cm ³	1.6 ± 0.01						
Composite (70/30)							
Thermal diffusivity, mm ² /s	0.254 ± 0.003	0.26 ± 0.002	0.256 ± 0.001	0.247 ± 0.002	0.235 ± 0.001	0.219 ± 0.001	0.197 ± 0.002
Thermal conductivity, W·m ⁻¹ ·K ⁻¹	0.539 ± 0.01	0.580 ± 0.01	0.609 ± 0.02	0.622 ± 0.02	0.631 ± 0.03	0.6402 ± 0.01	0.680 ± 0.02
Heat capacity, J/(g·K)	0.59 ± 0.02	0.61 ± 0.02	0.661 ± 0.02	0.70 ± 0.02	0.752 ± 0.02	0.815 ± 0.02	0.959 ± 0.02
Sample density, g/cm ³	3.6 ± 0.01						
Composite (50/50)							
Thermal diffusivity, mm ² /s	0.151 ± 0.005	0.178 ± 0.005	0.171 ± 0.004	0.164 ± 0.002	0.152 ± 0.002	0.144 ± 0.005	0.141 ± 0.007
Thermal conductivity, W·m ⁻¹ ·K ⁻¹	0.271 ± 0.01	0.330 ± 0.02	0.298 ± 0.01	0.300 ± 0.03	0.293 ± 0.01	0.294 ± 0.01	0.3 ± 0.01
Heat capacity, J/(g·K)	0.621 ± 0.02	0.641 ± 0.02	0.602 ± 0.02	0.631 ± 0.02	0.666 ± 0.02	6.706 ± 0.02	0.73 ± 0.02
Sample density, g/cm ³	2.9 ± 0.01						
Composite (30/70)							
Thermal diffusivity, mm ² /s	0.094 ± 0.008	0.109 ± 0.002	0.104 ± 0.004	0.098 ± 0.007	0.09 ± 0.003	0.082 ± 0.002	0.072 ± 0.005
Thermal conductivity, W·m ⁻¹ ·K ⁻¹	0.147 ± 0.02	0.171 ± 0.03	0.163 ± 0.01	0.157 ± 0.01	0.148 ± 0.02	0.141 ± 0.04	0.145 ± 0.01
Heat capacity, J/(g·K)	0.602 ± 0.02	0.604 ± 0.02	0.605 ± 0.02	0.619 ± 0.02	0.634 ± 0.02	0.666 ± 0.02	0.775 ± 0.02
Sample density, g/cm ³	2.6 ± 0.01						
Metallic Glass							
Thermal diffusivity, mm ² /s	0.462 ± 0.013	0.466 ± 0.004	0.479 ± 0.003	0.487 ± 0.003	0.499 ± 0.002	0.505 ± 0.007	0.503 ± 0.005
Thermal conductivity, W·m ⁻¹ ·K ⁻¹	2.41 ± 0.1	2.48 ± 0.1	2.80 ± 0.1	2.92 ± 0.1	3.17 ± 0.2	3.46 ± 0.2	4.10 ± 0.3

Table 1. Cont.

Temperature Analysis, °C	25	50	100	150	200	250	300
Heat capacity, J/(g·K)	1.024 ± 0.02	1.044 ± 0.02	1.149 ± 0.02	1.177 ± 0.02	1.249 ± 0.02	1.347 ± 0.02	1.599 ± 0.02
Sample density, g/cm ³	5.1 ± 0.01						

3.5. Scanning Electron Microscope

SEM analysis was performed to study the microstructure of the composite. Figure 5 shows that the bonding between the particles was not adequate. The presence of coarse metallic glass particles and PTFE can also be seen in the microstructure images. These influenced the resulting properties of the composites.

Figure 5. SEM images of (a) 30/70 composite and (b) 50/50 composite.

4. Discussions

The XRD pattern of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass shows a broad halo between the diffraction angles of $2\theta \approx 38^\circ$ to 50° , without any sharp diffraction peaks. This indicates the amorphous behavior of the metallic glass. After ball milling of the metallic glass, a broad halo spectrum indicates the amorphous nature of the sample. During SPS, some crystalline peaks occurred, which corresponded to the formation of crystalline precipitates. Zr_2Ni and Zr_2Cu were indexed as the crystalline phase. In [50], the authors showed that metallic glass is semicrystalline. It should also be noted that after SPS at 400°C , the crystalline phase (Table 2) was increased to $30 \pm 5\%$ in the MG sample.

Table 2. Phase composition of the obtained samples.

Phase Composition	$\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$	$\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ after BM	$\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ after SPS
Amorphous	100%	100%	$70 \pm 15\%$
$\text{Zr}_2\text{Ni} + \text{Zr}_2\text{Cu}$	-	-	$\approx 30 \pm 5\%$

The most intense crystalline peaks in the polymer samples correspond to the PTFE. The metallic glass was mixed with a polymer, and different proportions of the composite samples were prepared. The crystalline peaks corresponded to the PTFE for all composite samples. A broad halo diffraction spectrum similar to the metallic glass at $2\theta = 38^\circ$ to 50° was visible in the composite samples, which showed their amorphous nature. There was the formation of Zr_2Cu in the composite samples, but this was not seen in different XRD intensity peaks. The sizes of this Zr_2Cu should be nanocrystalline, but the amount of this phase should not be more than 5%.

The DSC scan of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ metallic glass shows it was heated at 10 K/min. The onset glass transition temperature (T_g) is 374 °C, and the onset crystallization transition temperature (T_x) is 461 °C. The supercooled region $T_{sc} = T_x - T_g$ is 87 °C. Zr-based metallic glass has high thermal stability, which leads to a stable supercooled region [51]. PTFE and 30/70, 50/50 and 70/30 composites were heated at 10K/min. The composites have a melting temperature near PTFE. This result is similar to our previous research [43]. The thermal conductivity of the metallic glass is higher than the other samples and results in a decrease in the melting point of the composites. During DSC heating, the composites start to melt faster (with increasing MG content) when heat is transferred to the metallic glass. Hence, the melting peaks of the composite start to shift toward PTFE. Senatov et al. [52] showed that the dispersed filler in the polymer is influenced by the melting point of the polymer. The above factors could affect the melting point of the composites. Structural relaxation [53] is an important aspect of metallic glass. This is caused due to the change in the microstructure. It normally occurs near the glass transition (T_g) of the metallic glass. When heat is given to metallic glass, a local rearrangement of atoms occurs for a short-range order leading to a nonhomogenous region. This causes fluctuation in the electron density. These fluctuations are a result of structural relaxation during heating and can be seen in composites.

Dynamic mechanical properties were used to study the structural evolution of the sample. Storage modulus (E') and loss factor ($\tan \delta$) were examined under constant heating and different frequencies (0.1 Hz, 1 Hz and 10 Hz). $\tan \delta$ or internal friction was used to measure the relaxation process in the samples. For the metallic glass, the storage modulus is constant up to 115 °C. It increases from 115 °C to 311 °C at 10 Hz, to 270 °C at 1 Hz and 246 °C to 0.1 Hz. There is a decrease in the storage modulus near the super liquid region. This is associated with a decrease in the viscosity and solid to liquid behavior translation takes place. During this process, mechanical relaxation occurs and is defined by viscoelastic loss [54]. The internal friction ($\tan \delta$) increases with an increase in temperature. The storage modulus of the PTFE decreases with temperature due to the mechanical losses that occur during the secondary relaxation [55]. The local movement of the polymeric chains affects the mechanical rigidity of PTFE [56]. For PTFE, at 0.1Hz and 1 Hz, there is α transition from 130 to 145°C. The other peaks correspond to the glassy phase of PTFE. At 10 Hz, α transition occurring from 130 to 145 °C could be seen. The storage modulus of the 30/70, 50/50 and 70/30 samples was decreased with an increase in temperature. The mobility of the PTFE increases with an increase in temperature as it goes from the glass state to the viscous flow. This increases the deformation state of the composite [57]. The storage modulus of 70/30 is highest among the 30/70 and 50/50 composite samples. This can be attributed to the increase in the metallic glass content. For composite samples, the loss factor with frequencies 0.1 Hz and 1 Hz increases with an increase in temperature. For 10 Hz, the loss factor decreases with an increase in temperature. The α transition peak at 130–145 °C could be seen in all the composites similar to the PTFE. Another peak in the composites around 350 °C shows the melting of the polymer. The PTFE peaks represent β -relaxation before α relaxation. The composites have similar peaks to PTFE and can be explained by the PTFE peaks [58].

Metallic glass has the highest thermal conductivity, and PTFE has the least thermal conductivity among samples. The thermal conductivity of the metallic glass is temperature dependent and increases with an increase in temperature. Heat transfer is influenced by the lattice structure. Thermal diffusivity is dependent on the temperature and related to the mean free path changes. The translation enthalpy causes a change in the structure of the PTFE. This reduces the thermal conductivity of the PTFE at higher temperatures [59]. The 70/30 composite has the most thermal conductivity between the 50/50 and 30/70 composites. This is because the composite has more metallic glass content. The 70/30 composite shows an increase in conductivity with temperature. The 50/50 composite has slightly more thermal conductivity compared to the 30/70 composite. The change in thermal conductivity in the 30/70 composite and 50/50 composite is due to the change in

the structure of the PTFE during the enthalpy process. This concludes that the addition of metallic glass into PTFE can improve the thermal conductivity of the composite.

The morphology of the composites was studied. Coarse particles, the presence of voids and lack of bonding result in the degradation of the properties of the composites. In this regard, it will be better to use organofunctional lubricants (for example, silanes) before the mechanical mixing of polymers and metallic glass. This will help to increase the interaction between the particles and improve interface bonding [40]. Additionally, for composite preparation, it will be better to use small glass particles with similar sizes to avoid varied particle sizes (especially coarse particles).

5. Conclusions

In the present study, metallic glass ($\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$) and PTFE composites were produced by ball milling. Different composites (30/70, 50/50 and 70/30) were prepared. Spark plasma sintering was used to produce a sample from metallic glass powder. It showed the formation of intermetallic crystalline Zr_2Ni and Zr_2Cu in the amount of about 30% for the MG sample. DMA was used to study the storage modulus and internal friction during heating of the samples. The storage modulus of the composites was decreased with an increase in temperature due to the increase in the mobility of the PTFE. α -structural relaxation occurred in the composites. The 70/30 composite had the highest thermal conductivity among the composite samples. The obtained composites will be promising in the field of dielectric materials for thermal applications.

Author Contributions: A.S. (Adit Sharma) analyzed the data, wrote, reviewed, and edited the manuscript; A.S. (Adit Sharma), M.Z., A.S. (Andrei Stepashkin), A.K. (Aksar Kvaratskheliya), A.K. (Artem Korol), D.M., S.K. and V.Z. conceived and designed the experiments. All authors have read and agreed to the published version of the manuscript.

Funding: The reported study was funded by RFBR, Project N20-32-90041. M.Z. gratefully acknowledges the financial support made within the Ministry of Science and Higher Education of the Russian Federation in the framework of the Increase Competitiveness Program of NUST “MISiS” (Grant Number K3-2015-036).

Data Availability Statement: Data presented in this article are available at request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Telford, M. The case for bulk metallic glass. *Mater. Today* **2004**, *7*, 36–43. [\[CrossRef\]](#)
2. Sheng, H.W.; Luo, W.K.; Alamgir, F.M.; Bai, J.M.; Ma, E. Atomic packing and short-to-medium-range order in metallic glasses. *Nature* **2006**, *439*, 419–425. [\[CrossRef\]](#)
3. Ashby, M.F.; Greer, A.L. Metallic glasses as structural materials. *Scr. Mater.* **2006**, *54*, 321–326. [\[CrossRef\]](#)
4. Schuh, C.A.; Hufnagel, T.C.; Ramamurty, U. Mechanical behavior of amorphous alloys. *Acta Mater.* **2007**, *55*, 4067–4109. [\[CrossRef\]](#)
5. Greer, A.L.; Cheng, Y.Q.; Ma, E. Shear bands in metallic glasses. *Mater. Sci. Eng. R Rep.* **2013**, *74*, 71–132. [\[CrossRef\]](#)
6. Jang, B.Z.; Uhlmann, D.R.; Sande, J.B.V. Ductile–brittle transition in polymers. *J. Appl. Polym. Sci.* **1984**, *29*, 3409–3420. [\[CrossRef\]](#)
7. Sanchez, C.; Julián, B.; Belleville, P.; Popall, M. Applications of hybrid organic-inorganic nanocomposites. *J. Mater. Chem.* **2005**, *15*, 3559–3592. [\[CrossRef\]](#)
8. Lee, J.; Huang, K.H.; Hsu, K.C.; Tung, H.C.; Lee, J.W.; Duh, J.G. Applying composition control to improve the mechanical and thermal properties of Zr-Cu-Ni-Al thin film metallic glass by magnetron DC sputtering. *Surf. Coat. Technol.* **2015**, *278*, 132–137. [\[CrossRef\]](#)
9. Korkmaz, S.; Kariper, A. Glass formation, production and superior properties of Zr-based thin film metallic glasses (TFMGs): A status review. *J. Non. Cryst. Solids* **2020**, *527*. [\[CrossRef\]](#)
10. Tang, C.; Li, Y.; Zeng, K. Characterization of mechanical properties of a Zr-based metallic glass by indentation techniques. *Mater. Sci. Eng. A* **2004**, *384*, 215–223. [\[CrossRef\]](#)
11. Khan, M.M.; Deen, K.M.; Haider, W. Combinatorial development and assessment of a Zr-based metallic glass for prospective biomedical applications. *J. Non. Cryst. Solids* **2019**, *523*, 119544. [\[CrossRef\]](#)

12. Huang, L.; Pu, C.; Fisher, R.K.; Mountain, D.J.H.; Gao, Y.; Liaw, P.K.; Zhang, W.; He, W. A Zr-based bulk metallic glass for future stent applications: Materials properties, finite element modeling, and in vitro human vascular cell response. *Acta Biomater.* **2015**, *25*, 356–368. [\[CrossRef\]](#)
13. Chu, J.P.; Lee, C.M.; Huang, R.T.; Liaw, P.K. Zr-based glass-forming film for fatigue-property improvements of 316L stainless steel: Annealing effects. *Surf. Coat. Technol.* **2011**, *205*, 4030–4034. [\[CrossRef\]](#)
14. Wang, Q.; Qiang, J.B.; Xia, J.H.; Wu, J.; Wang, Y.M.; Dong, C. Cu-Zr-Al (Ti) bulk metallic glasses: Cluster selection rules and glass formation. *Intermetallics* **2007**, *15*, 711–715. [\[CrossRef\]](#)
15. Chu, C.W.; Jang, J.S.C.; Chen, G.J.; Chiu, S.M. Characteristic studies on the Zr-based metallic glass thin film fabricated by magnetron sputtering process. *Surf. Coat. Technol.* **2008**, *202*, 5564–5566. [\[CrossRef\]](#)
16. Chu, J.P.; Jang, J.S.C.; Huang, J.C.; Chou, H.S.; Yang, Y.; Ye, J.C.; Wang, Y.C.; Lee, J.W.; Liu, F.X.; Liaw, P.K.; et al. Thin film metallic glasses: Unique properties and potential applications. *Thin Solid Films* **2012**, *520*, 5097–5122. [\[CrossRef\]](#)
17. Hofmann, D.C.; Kozachkov, H.; Khalifa, H.E.; Schramm, J.P.; Demetriou, M.D.; Vecchio, K.S.; Johnson, W.L. Semi-solid induction forging of metallic glass matrix composites. *JOM* **2009**, *61*, 11–17. [\[CrossRef\]](#)
18. Chen, P.S.; Chen, H.W.; Duh, J.G.; Lee, J.W.; Jang, J.S.C. Characterization of mechanical properties and adhesion of Ta-Zr-Cu-Al-Ag thin film metallic glasses. *Surf. Coat. Technol.* **2013**, *231*, 332–336. [\[CrossRef\]](#)
19. Chuang, C.Y.; Liao, Y.C.; Lee, J.W.; Li, C.L.; Chu, J.P.; Duh, J.G. Electrochemical characterization of Zr-based thin film metallic glass in hydrochloric aqueous solution. *Thin Solid Films* **2013**, *529*, 338–341. [\[CrossRef\]](#)
20. Tsai, P.H.; Lin, Y.Z.; Li, J.B.; Jian, S.R.; Jang, J.S.C.; Li, C.; Chu, J.P.; Huang, J.C. Sharpness improvement of surgical blade by means of ZrCuAlAgSi metallic glass and metallic glass thin film coating. *Intermetallics* **2012**, *31*, 127–131. [\[CrossRef\]](#)
21. Chiang, P.T.; Chen, G.J.; Jian, S.R.; Shih, Y.H.; Jang, J.S.C.; Lai, C.H. Surface antimicrobial effects of Zr₆₁Al_{17.5}Ni₁₀Cu_{17.5}Si₄ thin film metallic glasses on *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Acinetobacter baumannii* and *Candida albicans*. *Food J. Health Sci.* **2010**, *2*, 12–20. [\[CrossRef\]](#)
22. Chu, J.P.; Liu, T.Y.; Li, C.L.; Wang, C.H.; Jang, J.S.C.; Chen, M.J.; Chang, S.H.; Huang, W.C. Fabrication and characterizations of thin film metallic glasses: Antibacterial property and durability study for medical application. *Thin Solid Films* **2014**, *561*, 102–107. [\[CrossRef\]](#)
23. Shen, J.; Zou, J.; Ye, L.; Lu, Z.P.; Xing, D.W.; Yan, M.; Sun, J.F. Glass-forming ability and thermal stability of a new bulk metallic glass in the quaternary Zr-Cu-Ni-Al system. *J. Non. Cryst. Solids* **2005**, *351*, 2519–2523. [\[CrossRef\]](#)
24. Chu, J.H.; Lee, J.; Chang, C.C.; Chan, Y.C.; Liou, M.L.; Lee, J.W.; Jang, J.S.C.; Duh, J.G. Antimicrobial characteristics in Cu-containing Zr-based thin film metallic glass. *Surf. Coat. Technol.* **2014**, *259*, 87–93. [\[CrossRef\]](#)
25. Ebnesajjad, S. Properties, Characteristics, and Applications of Expanded PTFE (ePTFE) Products. In *Expanded PTFE Applications Handbook*; William Andrew: Norwich, NY, USA, 2017; pp. 163–170. [\[CrossRef\]](#)
26. Luo, W.; Liu, Q.; Li, Y.; Zhou, S.; Zou, H.; Liang, M. Enhanced mechanical and tribological properties in polyphenylene sulfide/polytetrafluoroethylene composites reinforced by short carbon fiber. *Compos. Part B Eng.* **2016**, *91*, 579–588. [\[CrossRef\]](#)
27. Su, F.H.; Zhang, Z.Z.; Liu, W.M. Study on the friction and wear properties of glass fabric composites filled with nano- and micro-particles under different conditions. *Mater. Sci. Eng. A* **2005**, *392*, 359–365. [\[CrossRef\]](#)
28. Burkarter, E.; Saul, C.K.; Thomazi, F.; Cruz, N.C.; Roman, L.S.; Schreiner, W.H. Superhydrophobic electrosprayed PTFE. *Surf. Coat. Technol.* **2007**, *202*, 194–198. [\[CrossRef\]](#)
29. Li, J. Mechanical properties of a polyamide 6-RE in forced ptfе com posite. *Mech. Compos. Mater.* **2009**, *45*, 435–442. [\[CrossRef\]](#)
30. Cai, J.; Nesterenko, V.F.; Vecchio, K.S.; Jiang, F.; Herbold, E.B.; Benson, D.J.; Addiss, J.W.; Walley, S.M.; Proud, W.G. The influence of metallic particle size on the mechanical properties of polytetrafluoroethylene-Al-W powder composites. *Appl. Phys. Lett.* **2008**, *92*, 26–29. [\[CrossRef\]](#)
31. Zaporojchenko, V.; Podschun, R.; Schürmann, U.; Kulkarni, A.; Faupel, F. Physico-chemical and antimicrobial properties of co-sputtered Ag-Au/PTFE nanocomposite coatings. *Nanotechnology* **2006**, *17*, 4904–4908. [\[CrossRef\]](#)
32. Kim, J.Y.; Gu, X.; Wraith, M.; Uhl, J.T.; Dahmen, K.A.; Greer, J.R. Suppression of catastrophic failure in metallic glass-polyisoprene nanolaminate containing nanopillars. *Adv. Funct. Mater.* **2012**, *22*, 1972–1980. [\[CrossRef\]](#)
33. Li, S.; Louzguine-Luzgin, D.V.; Xie, G.; Sato, M.; Inoue, A. Development of novel metallic glass/polymer composite materials by microwave heating in a separated H-field. *Mater. Lett.* **2010**, *64*, 235–238. [\[CrossRef\]](#)
34. Lasheras, A.; Gutiérrez, J.; Reis, S.; Sousa, D.; Silva, M.; Martins, P.; Lanceros-Mendez, S.; Barandiarán, J.M.; Shishkin, D.A.; Potapov, A.P. Energy harvesting device based on a metallic glass/PVDF magnetoelectric laminated composite. *Smart Mater. Struct.* **2015**, *24*, 065024. [\[CrossRef\]](#)
35. Gizaw, E.T.; Yeh, H.H.; Chu, J.P.; Hu, C.C. Fabrication and characterization of nitrogen selective thin-film metallic glass/polyacrylonitrile composite membrane for gas separation. *Sep. Purif. Technol.* **2020**, *237*, 116340. [\[CrossRef\]](#)
36. Venkataraman, S.; Rozhkova, E.; Eckert, J.; Schultz, L.; Sordet, D.J. Thermal stability and crystallization kinetics of Cu-reinforced Cu₄₇Ti₃₃Zr₁₁Ni₈Si₁ metallic glass composite powders synthesized by ball milling: The effect of particulate reinforcement. *Intermetallics* **2005**, *13*, 833–840. [\[CrossRef\]](#)
37. Lee, K.S.; Kang, S.H.; Lee, Y.S. Synthesis of Zr-based bulk metallic glass-crystalline aluminum alloy composite by co-extrusion. *Mater. Lett.* **2010**, *64*, 129–132. [\[CrossRef\]](#)
38. Kündig, A.A.; Schweizer, T.; Schafner, E.; Löffler, J.F. Metallic glass/polymer composites by co-processing at similar viscosities. *Scr. Mater.* **2007**, *56*, 289–292. [\[CrossRef\]](#)

39. Nieh, T.G.; Wadsworth, J.; Liu, C.T.; Ohkubo, T.; Hirotsu, Y. Plasticity and structural instability in a bulk metallic glass deformed in the supercooled liquid region. *Acta Mater.* **2001**, *49*, 2887–2896. [\[CrossRef\]](#)
40. Zadorozhnyy, M.Y.; Chukov, D.I.; Churyukanova, M.N.; Gorshenkov, M.V.; Zadorozhnyy, V.Y.; Stepashkin, A.A.; Tsarkov, A.A.; Louzguine-Luzgin, D.V.; Kaloshkin, S.D. Investigation of contact surfaces between polymer matrix and metallic glasses in composite materials based on high-density polyethylene. *Mater. Des.* **2016**, *92*, 306–312. [\[CrossRef\]](#)
41. Zadorozhnyy, V.Y.; Gorshenkov, M.V.; Churyukanova, M.N.; Zadorozhnyy, M.Y.; Stepashkin, A.A.; Moskovskikh, D.O.; Ketov, S.V.; Zinnurova, L.K.; Sharma, A.; Louzguine-Luzgin, D.V.; et al. Investigation of structure and thermal properties in composite materials based on metallic glasses with small addition of polytetrafluoroethylene. *J. Alloys Compd.* **2017**, *707*, 264–268. [\[CrossRef\]](#)
42. Zadorozhnyy, V.; Churyukanova, M.; Stepashkin, A.; Zadorozhnyy, M.; Sharma, A.; Moskovskikh, D.; Wang, J.; Shabanova, E.; Ketov, S.; Louzguine-Luzgin, D.; et al. Structure and thermal properties of an Al-based metallic glass-polymer composite. *Metals* **2018**, *8*, 1037. [\[CrossRef\]](#)
43. Sharma, A.; Kopylov, A.; Zadorozhnyy, M.; Stepashkin, A.; Kudelkina, V.; Wang, J.Q.; Ketov, S.; Churyukanova, M.; Louzguine-Luzgin, D.; Sarac, B.; et al. New Mg-Based Metallic Glass-Polymer Composites: Investigation of Structure, Thermal Properties, and Biocompatibility. *Metals* **2020**, *10*, 867. [\[CrossRef\]](#)
44. Orrù, R.; Licheri, R.; Locci, A.M.; Cincotti, A.; Cao, G. Consolidation/synthesis of materials by electric current activated/assisted sintering. *Mater. Sci. Eng. R Rep.* **2009**, *63*, 127–287. [\[CrossRef\]](#)
45. Shelekhov, E.V.; Sviridova, T.A. Programs for x-ray analysis of polycrystals. *Met. Sci. Heat Treat.* **2000**, *42*, 309–313. [\[CrossRef\]](#)
46. Wagner, M. *Thermal Analysis in Practice*; Carl Hanser Verlag GmbH Co KG: Munich, Germany, 2017; pp. 1–9. [\[CrossRef\]](#)
47. He, L.; Wu, Z.G.; Jiang, F.; Sun, J. Enhanced thermal stability of Zr₆₅Cu_{17.5}Ni₁₀Al_{7.5} metallic glass at temperature range near glass transition by oxygen impurity. *J. Alloys Compd.* **2008**, *456*, 181–186. [\[CrossRef\]](#)
48. Abrosimova, G.E.; Aronin, A.S.; Kir'janov, Y.V.; Matveev, D.V.; Molokanov, V.V.; Zver'kova, I.I. Crystalline layer on the surface of Zr-based bulk metallic glasses. *J. Non. Cryst. Solids.* **2001**, *288*, 121–126. [\[CrossRef\]](#)
49. Qiao, J.C.; Pelletier, J.M. Influence of thermal treatments and plastic deformation on the atomic mobility in Zr_{50.7}Cu₂₈Ni₉Al_{12.3} bulk metallic glass. *J. Alloys Compd.* **2015**, *615*, S85–S89. [\[CrossRef\]](#)
50. Mihaylov, L.; Lyubenova, L.; Gerdjikov, T.; Nihtianova, D.; Spassov, T. Selective dissolution of amorphous Zr-Cu-Ni-Al alloys. *Corros. Sci.* **2015**, *94*, 350–358. [\[CrossRef\]](#)
51. Wang, Q.; Liu, C.T.; Yang, Y.; Dong, Y.D.; Lu, J. Atomic-scale structural evolution and stability of supercooled liquid of a Zr-based bulk metallic glass. *Phys. Rev. Lett.* **2011**, *106*, 1–4. [\[CrossRef\]](#)
52. Senatov, F.; Niaza, K.; Zadorozhnyy, V.Y.; Maksimkin, A.; Kaloshkin, S.; Estrin, Y. Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds. *J. Mech. Behav. Biomed. Mater.* **2016**, *57*, 139–148. [\[CrossRef\]](#)
53. Aji, D.P.; Mujalis, Y. Physical Aging of Zr₆₅Cu_{17.5}Ni₁₀Al_{7.5} Glassy Alloy. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *547*, 012036. [\[CrossRef\]](#)
54. Qiao, J.C.; Casalini, R.; Pelletier, J.M.; Yao, Y. Dynamics of the strong metallic glass Zn₃₈Mg₁₂Ca₃₂Yb₁₈. *J. Non. Cryst. Solids* **2016**, *447*, 85–90. [\[CrossRef\]](#)
55. Calleja, G.; Jourdan, A.; Ameduri, B.; Habas, J.P. Where is the glass transition temperature of poly(tetrafluoroethylene)? A new approach by dynamic rheometry and mechanical tests. *Eur. Polym. J.* **2013**, *49*, 2214–2222. [\[CrossRef\]](#)
56. Aharoni, S.M. Molecular stiffness and thermal properties of polymers. *J. Appl. Polym. Sci.* **1976**, *20*, 2863–2869. [\[CrossRef\]](#)
57. Wu, J.; Wang, H.; Feng, B.; Li, Y.; Wu, S.; Yin, Q.; Yu, Z.; Huang, J. The effect of temperature-induced phase transition of PTFE on the dynamic mechanical behavior and impact-induced initiation characteristics of Al/PTFE. *Polym. Test.* **2020**, *91*, 106835. [\[CrossRef\]](#)
58. Henri, V.; Dantras, E.; Lacabanne, C.; Dieudonne, A.; Koliatene, F. Thermal ageing of PTFE in the melted state: Influence of interdiffusion on the physicochemical structure. *Polym. Degrad. Stab.* **2020**, *171*, 109053. [\[CrossRef\]](#)
59. Price, D.M.; Jarratt, M. Thermal conductivity of PTFE and PTFE composites. *Thermochim. Acta* **2002**, *392–393*, 231–236. [\[CrossRef\]](#)