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Crystallization Kinetics of 50% W Particles/Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} Metallic Glass Matrix Composite

Xiaohong Su, Huie Hu * , Xiaodong Kong and Zhou Lu

Department of Basic Course, Naval University of Engineering, Wuhan 430033, China; surrey0908@outlook.com (X.S.); kxd63813@hotmail.com (X.K.); frankykyyy@outlook.com (Z.L.)

* Correspondence: huhuie_nue@outlook.com; Tel.: +86-276-546-0494

Received: 14 October 2018; Accepted: 27 November 2018; Published: 2 December 2018

Abstract: The crystallization kinetics of the 50% W particles/Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} metallic glass matrix composite were studied by differential scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). The results showed that the crystallization and the glass transition of the composite both have a kinetic effect. The characteristic temperatures T_g and T_x of the composite are linearly related to the natural logarithm of the heating rate ($\ln\phi$), and the presence of W particles increases the dependence of the glass transition on the heating rate. With the addition of W particles, the viscosity of the amorphous matrix in the supercooled liquid region increases, which hinders the spread and migration of the alloy elements and causes the thermal stability of the supercooled liquid to improve. In the isothermal crystallization, the mode of nucleation and the growth process of the crystal changes with the annealing temperature. The Avrami exponent with the crystallized fraction at 698 K was about 2.5 in the middle stage of the crystallization, implying three-dimensional growth with a constant nucleation rate.

Keywords: crystallization kinetics; W particles; metallic glass matrix composite; thermal stability

1. Introduction

The important application value of Zr-based bulk metallic glass (BMG) can be attributed to its unique properties, such as high strength, high hardness, self-sharpening, and good corrosion resistance [1–7], but its brittleness at room temperature limits its further application. Currently, the main solution to the brittleness is improving the room temperature plasticity of BMG via the in situ or ex situ introduction of appropriate second phases to the amorphous matrix to obtain bulk metallic glass matrix composite (BMGMC), which has been widely researched [8–15]. The addition of plastic W into Zr-based metallic glass can significantly improve its comprehensive mechanical properties and penetrating capability, so the W/Zr based metallic glass composite has been considered to have good application prospects in weapons such as armored bombs [16,17]. Therefore, much research has been conducted on W/Zr-based metallic glass composites [18–24]. Conner et al. studied the mechanical properties of a tungsten fiber-reinforced Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni₁₀Be_{22.5} metallic glass matrix composite and found that tungsten reinforcement increases the compressive strain to failure by over 900% compared to the unreinforced Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni₁₀Be_{22.5} [18]. Xue et al. introduced a Zr-based BMGMC by infiltrating the Zr₃₈Ti₁₇Cu_{10.5}Co₁₂Be_{22.5} melt into porous tungsten and studied the dynamic mechanism of fracture and deformation behavior of this composite [21]. Qiu and his team prepared 60 vol.% W particles-reinforced Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} BMGMC and reported that the plasticity and dynamic compression strength for the composite both increased when W particles were

added [23]. The crystallization kinetics of the W/Zr-based metallic glass composite in the supercooled liquid phase plays an important role in the superplastic formation and application of the composite. However, relevant studies have not been reported to date.

As an ideal amorphous material, the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ alloy has a strong glass-forming ability and good thermal stability [25], which is suitable for matrix material. In this paper, the 50% W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite was prepared, and the crystallization kinetics of the material were studied by X-ray diffraction (XRD), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), and differential scanning calorimetry (DSC).

2. Materials and Methods

Ingots of the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ master alloy were prepared by arc melting a mixture of the elements having a purity of 99.95 at.% or better. Subsequently, the pre-alloyed ingots were ground into powder and then the pre-alloyed powder and the 50 vol.% W particles (200–700 μm in size, purity of 99%) were mixed by ball milling for 5 min under argon gas protection. The mixing powder was pressed into a lump, and the lump was loaded into a steel tube with a diameter of 6 mm at a vacuum degree of 1×10^{-3} Pa. The steel tube was then quickly introduced into a resistance furnace at 1370 K and kept for 5 min, and finally the steel tube was quenched in saturated brine [23].

The $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass and the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite were cut into $\Phi 3 \times 0.5$ mm sheets by wire-cutting, and polished using metallographic paper for DSC (Mettler–Toledo TGA/DSC 1, METTLER TOLEDO, Zurich, Switzerland) tests. The structure of the materials was identified by XRD (Cu $K\alpha$ radiation, Philips X'pert PRO, Philips Japan, Ltd., Tokyo, Japan) and SEM combined with EDS (QUANTA 400, FEI, Eindhoven, Netherlands). Five points were selected for EDS and the error of the result was less than 5%. DSC measurements were performed under a constant flow of high-purity Ar, the non-isothermal DSC was carried out from 298 K to 923 K at heating rates ranging from 10 to 80 K/min, and the isothermal DSC was carried out at various temperatures in the supercooled liquid region for 60 min. In order to reduce the measurement error, three replicas were performed for each heating rate.

3. Results and Discussion

3.1. Structure

The XRD patterns of the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass and the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite are shown in Figure 1. The typical scattering diffusion peak is found from the curve of the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ BMG, which indicates an amorphous structure of the material. Apart from the characteristic diffraction peak of W and the amorphous scattering diffusion peak, no other crystalline-phase diffraction peaks are observed in the curve of the composite, implying that the amorphous matrix and the W particles retain their original structures.

The SEM micrograph of the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite is shown in Figure 2a,c, in which the white W particles are evenly dispersed in the black metallic glass matrix. At the same time, there are no reaction layers in the interface between the W particles and the amorphous matrix. According to the EDS spectrum (Figure 2b) of the black metallic glass matrix in region A, the W content of 0.36% in the amorphous matrix indicates that the second-phase W atoms are partly dissolved into the amorphous matrix during the preparation of the composite. Similar results were reported in the W particles/ $\text{Zr}_{57}\text{Nb}_5\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$ metallic glass matrix composite [26].

Figure 1. The X-ray diffraction patterns of two materials (curve **a** corresponds to the metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, curve **b** corresponds to the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite).

Figure 2. SEM micrograph (**a,c**) and energy dispersive spectroscopy (EDS) spectrum (**b**) of the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite.

3.2. Crystallization Kinetics

The DSC curves at different heating rates of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass and the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite are shown in Figure 3. The DSC

curves for the two materials exhibit a distinct endothermic event at the characteristic temperatures for the glass transition T_g , the onset of crystallization T_x , the first crystallization peak T_{p1} , the second crystallization peak T_{p2} , and an extended supercooled liquid region ΔT . All the characteristic thermal parameters are listed in Table 1.

Figure 3. Differential scanning calorimetry (DSC) curves of two materials at different heating rates: (a) the metallic glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$; (b) the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite.

Table 1. T_g , T_x , ΔT , and T_p of the metallic glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ and the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite.

Material	Heating Rates	T_g (K)	T_x (K)	ΔT (K)	T_{p1} (K)	T_{p2} (K)
Metallic glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$	10 K/min	618 ± 0.5	682 ± 0.5	64	695 ± 0.5	726 ± 0.5
	20 K/min	622 ± 0.5	696 ± 0.5	74	714 ± 0.5	736 ± 0.5
	40 K/min	629 ± 0.5	715 ± 0.5	86	729 ± 0.5	748 ± 0.5
	80 K/min	640 ± 0.5	731 ± 0.5	91	744 ± 0.5	766 ± 0.5
W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite	10 K/min	613 ± 0.5	695 ± 0.5	82	712 ± 0.5	738 ± 0.5
	20 K/min	625 ± 0.5	716 ± 0.5	91	726 ± 0.5	750 ± 0.5
	40 K/min	633 ± 0.5	727 ± 0.5	94	740 ± 0.5	761 ± 0.5
	80 K/min	644 ± 0.5	740 ± 0.5	96	760 ± 0.5	779 ± 0.5

It is presented in Table 1 that all the characteristic temperatures T_g , T_x , and T_p of the metallic glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ and the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite move to high-temperature regions with an increase in the heating rate, and the error of the characteristic temperature is ± 0.5 K. The DSC results indicate that the crystallization behavior and glass transition behavior of the two materials both have a kinetic effect. In addition to this, the supercooled liquid regions ΔT for the composite is larger than that of the metallic glass, indicating that the thermal stability of the composite is improved [27,28].

The T_g and T_x curves of the metallic glass and the composite with respect to the heating rate φ are shown in Figure 4. The characteristic temperature T (including T_g and T_x of the two materials) is linearly related to $\ln \varphi$, and this relationship is called Lasocka's relationship [29], which can be written as follows:

$$T = A + B \ln \varphi \quad (1)$$

where T stands for the characteristic temperature, A and B are constants, and φ is the heating rate. The value of B reflects the dependence of T_g and T_x on the heating rate φ . The B values for the crystallization of the metallic glass and the composite are 23.95 (error of 0.93%) and 21.06 (error of 2.2%), respectively. However, the B values for the glass transition of the two materials are only 10.53 (error of 1.60%) and 14.57 (error of 1.13%), respectively. Therefore, the kinetic effect of crystallization is stronger than that of glass transition. In addition to this, the B value of 14.57 of the glass transition for the composite is greater than that of the metallic glass (10.53), indicating that the 50% W particles in the composite increase the dependence of the glass transitions on the heating rate.

Figure 4. Plots for T_g and T_x vs. $\ln \phi$ of two materials: (a) the metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$; (b) the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass composite.

The activation energy of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass and the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite in a continuous heating process can be obtained using the Kissinger equation, as follows:

$$\ln(T^2/\phi) = E/RT + C \quad (2)$$

where T stands for the characteristic temperature, ϕ is the heating rate, E is the activation energy, R is the gas constant, and C is a constant. The curves of $\ln(T^2/\phi)$ and $1/T$ of the corresponding characteristic temperatures at different heating rates are obtained and shown in Figure 5. By a linear fitting method, the activation energy for the glass transition E_g , the activation energy for the onset temperature of crystallization E_x , the activation energy for the first peak temperature of crystallization E_{p1} , and the activation energy for the second peak temperature of crystallization E_{p2} are calculated by the slope of the line, and the values of the activation energies are shown in Table 2. Table 2 shows that the activation energy for the glass transition of the composite is 213.4 kJ/mol, which is clearly lower than that of the metallic glass (288.8 kJ/mol). The reduction of the activation energy from the amorphous state to the supercooled liquid (glass transition) indicates that the barrier for the composite to overcome in the glass transition is lower than that of the metallic glass. At the same time, considering the experimental error, the crystallization activation energy for the onset crystallization (185.3 kJ/mol) of composites is similar to or even slightly above that of the metallic glass (161.8 kJ/mol), implying that the composite has a good thermal stability in the supercooled liquid region.

Figure 5. Kissinger plots for two materials at different heating rates: (a) the metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$; (b) the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite.

Table 2. E_g , E_x , and E_p of the metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite.

Material	E_g (kJ/mol)		E_x (kJ/mol)		E_{p1} (kJ/mol)		E_{p2} (kJ/mol)	
	Value	Error	Value	Error	Value	Error	Value	Error
Metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	288.8	5.28%	161.8	0.60%	170.5	1.15%	225.5	2.71%
W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite	213.4	1.51%	185.3	0.61%	172.7	1.17%	233.8	2.60%

It can be concluded from the above data that the thermal stability of the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite is improved, which may be related to the viscosity of the composite melt in the supercooled liquid region. With the addition of W particles, the viscosity of the composite in the supercooled liquid region increases, which hinders the spread and migration of the alloy elements, allowing the thermal stability of the supercooled liquid to be improved [30]. On the question of whether the 0.36% W atoms dissolved in the amorphous matrix affect the thermal stability of the composite, Choi-Yim et al. conducted a similar study and found that nearly 0.4% W dissolved in the amorphous matrix $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ bulk metallic glass, but the thermal stability of the matrix did not change after the addition of the W particles [26].

It was reported in Reference [31] that the influence of temperature on viscosity near the glass transition temperature can be expressed by the VTF (Vogel-Tamman-Fulcher) equation, and the viscosity decreases sharply with increasing the temperature. Thus, the E_g of the composite is lower than that of the metallic glass due to the increasing of the glass transition temperature. However, near the crystallization transition temperature, the viscosity of the supercooled liquid changes little with temperature, and the main influencing factor on viscosity is the addition of 50% W particles, so the E_x of the composite is similar to or even slightly above that of the metallic glass.

3.3. Isothermal Crystallization

The isothermal DSC curves of the W particles/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass matrix composite at various temperatures in the supercooled liquid region are shown in Figure 6. The crystallization reaction occurs in the amorphous matrix after a certain incubation time at different temperatures. The time–temperature–transformation (TTT) curve for onset crystallization is shown in Figure 7, and the curve starts with the time point of crystallization phase volume fraction of 1%. With the increase of annealing temperature, the incubation period of crystallization becomes shorter and the crystallization peak becomes lower and broader. The reduction of the incubation time indicates that the crystallization rate of the composite increases with increasing the crystallization temperature. Figure 8 shows the crystallized fraction x as a function of annealing time. The curves at various temperatures all show a typical “S” shape, implying that the crystallization pathway is typical nucleation and growth. It is presented that the crystallization volume fraction changes relatively slowly in the early stage of crystallization because the atoms in the solid state are unable to spread. With increasing the annealing time, the crystallization volume fraction rapidly increases. At the late stage of crystallization, the crystallization volume fraction changes very little with the annealing time because less and less amorphous phase remains.

Figure 6. Isothermal DSC curves at various temperatures for the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite.

Figure 7. Time-temperature-transformation curves of the onset crystallization for the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite.

Figure 8. Crystallization volume fraction as a function of holding time at different temperatures for the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite.

The isothermal crystallization kinetics of the W particles/Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} metallic glass matrix composite is modeled by the JMA (Johnson–Mehl–Avrami) equation:

$$\ln[-\ln(1-x)] = \ln k + n \ln(t - \tau) \quad (3)$$

where x is the crystallized volume fraction (%), n is the Avrami exponent reflecting the mode of nucleation and growth in the amorphous alloy during crystallization, k is a reaction rate constant, t is the holding time, and τ is the incubation time taken as the interval between the time when the materials reach the annealing temperature and the start of the transformation. The JMA plots of isothermal crystallization at different temperatures for the composite obtained by $\ln[-\ln(1-x)]$ vs. $\ln(t - \tau)$ ($20\% < x < 80\%$) are shown in Figure 9. The Avrami index n changes as the temperature changes, and the change of n reflects the constant change of the nucleation and growth process of the crystal [32]. At 698 K, n is close to 2.5 considering the experimental error, suggesting that the nucleation rate is constant and the growth of the crystal nucleus is controlled by diffusion. When the temperature is 703 K, $n = 2.7$, the nucleation rate increases with time, and the growth of the crystal nucleus is still controlled by diffusion. As the temperature rises to 708 K, $n = 3.0$, the growth of the crystal nucleus is controlled by the interface, and the nucleation rate is zero. As the temperature of isothermal crystallization continues to rise to 713 K, $3 < n < 4$, indicating that the growth of the crystal nucleus is still controlled by the interface, but the nucleation rate decreases with time [33,34].

Figure 9. JMA (Johnson–Mehl–Avrami) plots of crystallization at different temperatures for the W particles/Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} metallic glass matrix composite.

In order to investigate the details of the crystallization process, the local Avrami exponent $n(x)$ is calculated using the following equation [35]:

$$n(x) = \frac{\partial \ln[-\ln(1-x)]}{\partial \ln(t - \tau)} \quad (4)$$

The value of $n(x)$ gives information on the nucleation and growth behavior when the crystallized volume fraction is x . Figure 10 shows the change in the Avrami exponent with crystallized fraction at 698 K. The Avrami exponent in the initial stages of crystallization is close to 3. With an increasing crystallized volume fraction, the n steadily decreases and reaches 2, implying that the growth of the crystal nucleus is controlled by the interface, and the nucleation rate decreases with increasing the crystallized volume fraction. In the middle stage, covering a wide range of $20\% < x < 80\%$, the Avrami exponent tends to be 2.5, implying three-dimensional growth with a constant nucleation

rate; the observed increase in n at the last stage of crystallization may be due to errors derived from isothermal DSC.

Figure 10. Variation of the local Avrami exponent with crystallized volume fraction for the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite.

Figure 11 shows the X-ray diffraction patterns of the two materials after annealing at 703 K. The amorphous scattering diffusion peak of the amorphous matrix and the characteristic diffraction peaks of the W particles in curve a imply a fully amorphous structure of the matrix. After the incubation period in annealing at 703 K, the crystals precipitate out from the matrix, as shown in the X-ray diffraction pattern of the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite annealed at 703 K (curve b). Except the sharp peaks of the additional W particles, the locations of the other peaks are basically consistent with the peaks of the metallic glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (curve c). This implies that the crystalline phases are roughly the same for the metallic glass and the composite after annealing at 703 K for 60 min, and that the diffraction peak calibration mainly indicates the presence of ZrBe_2 , Zr_2Cu , and ZrCu .

Figure 11. The X-ray diffraction patterns of the materials (curve a corresponds to the metallic glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ annealed at 703 K, curve b corresponds to the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite annealed at 703 K, curve c corresponds to the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite as-cast).

4. Conclusions

(1) The crystallization and glass transition of the W particles/ $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass matrix composite both have a kinetic effect, and the characteristic temperatures T_g and T_x of the composite are linearly related to $\ln\phi$, as the 50% W particles in the composite increase the dependence of the glass transition on the heating rate.

(2) With the addition of W particles, the viscosity of the amorphous matrix in the supercooled liquid region increases, which hinders the spread and migration of the alloy elements and improves the thermal stability of the supercooled liquid.

(3) In the isothermal crystallization, the mode of the nucleation and growth process of crystal changes as the temperature changes from 698 K to 713 K. The Avrami exponent at 698 K was about 2.5 with the crystallized fraction in the middle stage ($20\% < x < 80\%$), implying three-dimensional growth with a constant nucleation rate, and the crystalline phases mainly indicated the presence of ZrBe_2 , Zr_2Cu , and ZrCu .

Author Contributions: Conceptualization, X.S., H.H.; Data curation, X.S.; Formal analysis, X.S., H.H., X.K.; Investigation, X.S., Z.L.; Project administration, H.H.; Writing—original draft, X.S.; Writing—review and editing, H.H., X.K.

Funding: This work was supported by the National Natural Science Foundation of China under Grant Nos.51575522 and the Basic Research Foundation of the Department of Basic Course in the Naval University of Engineering under Grant Nos.HGDJCB17ZK008.

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

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