

Article

Effect of Yttrium Doping on Glass-Forming Ability, Thermal Stability, and Corrosion Resistance of $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ Bulk Metallic Glass

Yuzhao Zhou ¹, Ling Zhao ¹, Yuwei Qu ^{1,2}, Liwei Hu ^{1,2}, Li Qi ², Fengsheng Qu ¹, Shixiong He ^{1,*} and Xue Liu ^{1,*} ¹ Institute of Materials, China Academy of Engineering Physics, Mianyang 621908, China² State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

* Correspondence: heshx2012@163.com (S.H.); xueliuthu@126.com (X.L.)

Abstract: Metallic glasses (MGs) possess excellent corrosion resistance due to their amorphous nature. Zr-Cu-Ni-Al is one of the most investigated metallic glass (MG) systems due to its excellent corrosion resistance, relatively low cost, and nontoxic qualities. Yet the application of the Zr-Cu-Ni-Al MGs is still limited by its glass forming ability (GFA). It has been found that the doping of yttrium can purify the Zr-Cu-Ni-Al melt and increase GFA. However, research on the yttrium doping's corrosion resistance is still lacking. In the present work, $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ ($x = 0$ (Y0), 1 (Y1), 2 (Y2), 3 (Y3)) alloys were prepared, and the effects of the yttrium doping on the thermodynamic parameters, crystallization activation energy, and corrosion resistance were studied. It was found that the doping of yttrium can improve the GFA and the crystallization-activation energy of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG. The largest GFA is obtained when the yttrium-doping content reaches 2 at.%. The parameter γ is found to be most suitable for the GFA evaluation of the $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ alloy system. Y2 alloy exhibits the best corrosion resistance among the Y0–Y3 alloys according to the potentiodynamic polarization results. The simultaneous increase of the GFA, thermal stability, and corrosion resistance was achieved in the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG by proper yttrium doping.

Keywords: metallic glasses; yttrium doping; glass forming ability; corrosion resistance

Citation: Zhou, Y.; Zhao, L.; Qu, Y.; Hu, L.; Qi, L.; Qu, F.; He, S.; Liu, X. Effect of Yttrium Doping on Glass-Forming Ability, Thermal Stability, and Corrosion Resistance of $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ Bulk Metallic Glass. *Metals* **2023**, *13*, 521. <https://doi.org/10.3390/met13030521>

Academic Editors: Golden Kumar and Sundeep Mukherjee

Received: 14 January 2023

Revised: 12 February 2023

Accepted: 21 February 2023

Published: 4 March 2023



Copyright: © 2023 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 glasses (MGs), which are also known as amorphous alloys, are believed to be a packing of long-range disordered atoms [1]. Due to their amorphous nature, MGs do not have the defects of dislocations, vacancies, and grain boundaries that are inevitable in conventional crystalline alloys [2]. In fact, the defects in MGs appear in the form of free volumes, which endow MGs with uniform and isotropic structures down to sub-nanometer scale [3]. The special amorphous structure of MGs give them excellent properties compared to the conventional crystalline alloys, such as high strength [1], high elastic limit [4], high fracture toughness [2,5], excellent wear resistance [6,7], excellent corrosion resistance [8–10], and excellent thermoplastic forming ability [11–13]. Among the above excellent properties, corrosion resistance is one of the most attractive advantages due to its wide potential applications [14]. The enhanced corrosion resistance of MGs commonly originates from two aspects: one is that the amorphous structure of MGs means they lack local electrochemical active sites, and the other one is that MGs have excellent composition-designable ability because they form solid solutions with beneficial alloying elements [1,15]. By trace doping of proper elements, the corrosion resistance of MGs can be significantly changed [15–17]. Thus, it is quite important to investigate the effect of elements doping on the corrosion resistance of MGs.

Up to now, various MGs have been developed, such as Pd-based [18], Ti-based [19], Zr-based [20], Fe-based [21], Ni-based [22], Mg-based MGs [23], and so on. Among the

developed MGs, Zr-Cu-Ni-Al is one of the most investigated alloy systems due to its excellent corrosion resistance, relatively low cost, and nontoxic qualities, and was found to be a promising candidate for corrosion-protective coatings [24,25]. However, the application as protective coatings remains a great challenge due to the limited glass-forming ability (GFA). The crystallization of the Zr-Cu-Ni-Al MGs will severely reduce its corrosion resistance. Huang et al. [26] found that a denser passive film can form on the surface of the Zr-Cu-Ni-Al MG, while the formation of a nanocrystalline phase in the MG matrix will reduce corrosion resistance. Hu et al. [24,27] further found that the pitting preferentially occurs at the crystalline area of the Zr-Cu-Ni-Al MG due to the enrichment of Cu. Thus, it is of great importance to improve the GFA of the Zr-Cu-Ni-Al MGs to guarantee excellent corrosion resistance.

It has been widely reported that the GFA of the Zr-Cu-Ni-Al MGs is quite sensitive to impurities, and that the presence of oxygen could have a significant adverse effect on the GFA [28–30]. It has been found that the doping of yttrium, which possesses significant affinity with oxygen, can purify the Zr-Cu-Ni-Al melt and increase its GFA [31–33]. For example, Hao et al. found that 0.5 at.% of yttrium addition can significantly suppress the precipitation of crystalline phases and enhance GFA in $\text{Ti}_{40}\text{Zr}_{25}\text{Be}_{20}\text{Cu}_{12}\text{Ni}_3$ amorphous alloy [34]. The doping of yttrium will also change the composition of the MGs. Since the corrosion resistance is closely related to the composition, the yttrium doping probably influences the corrosion resistance of the Zr-Cu-Ni-Al MGs. Besides that, new crystal phases will also form in the MG matrix when the yttrium is over-doped [35]. The newly formed phases may have an adverse effect on the corrosion behavior. Thus, the yttrium doping may affect the corrosion resistance of the Zr-Cu-Ni-Al MGs by changing the composition and the GFA.

However, research on the yttrium doping on the corrosion resistance of the Zr-based MGs is still lacking. In the present work, $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG [36] was selected as the research alloy; the effects of the yttrium doping on the thermodynamic parameters, crystallization activation energy, and corrosion resistance were studied. The simultaneous increase of the GFA, crystallization-activation energy, and corrosion resistance were achieved by proper yttrium doping in the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG. This work can greatly facilitate the final application of Zr-based MGs as corrosion-protective coatings.

2. Experimental Procedure

The $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ ($x = 0$ (Y0), 1 (Y1), 2 (Y2), 3 (Y3)) ingots were prepared by arc-melting in a Ti-gettered Ar atmosphere using high purity particles of Zr (99.5 wt.%), Cu (99.999 wt.%), Ni (99.99 wt.%), Al (99.999 wt.%), Y (99.99 wt.%) as raw materials. To ensure the chemical homogeneity of the prepared ingots, each alloy ingot was remelted six times with electromagnetic stirring. The remelted ingots were then sucked into a water-cooled Cu mold to obtain specimens with cylindrical steps as shown in Figure 1. The specimens comprise nine cylinders of different diameters. Each cylinder has a length of 10 mm. The maximum diameter of the cylinder is 9 mm and the minimum diameter is 1 mm. Contiguous cylinder-pairs have a difference in diameter of 1 mm.

To compare the GFA of the Y0, Y1, Y2, and Y3 alloys, the structure of the specimens was evaluated by X-ray diffraction (XRD) (Smartlab, Rigaku, Tokyo, Japan, $\text{Cu-K}\alpha$ radiation). Samples were cut off at the position of the $\Phi 6$ mm part of the specimens for XRD analysis. To guarantee that the specimens for thermodynamic property testing are fully amorphous, the top areas of the specimens with a diameter of 1 mm and a length of 2 mm were cut off, and differential scanning calorimetry (DSC) analysis was used for the thermodynamic property testing. Under the protection of high purity N_2 gas, the thermodynamic properties were tested using a DSC (NETZSCH, 200F3, Selb, Germany) analyzer at various heating rates of 10, 20, 40, and 60 $\text{K}\cdot\text{min}^{-1}$, with temperatures ranging from 298 K to 820 K. To reveal the melting temperature of the alloys, DSC (TA-Instruments, Q600, New Castle, DE, USA) measurements were also taken at a heating rate of 20 $\text{K}\cdot\text{min}^{-1}$ under the protection of high purity Ar gas, and the temperature ranged from 298 K to 1673 K.



Figure 1. Photograph of the Y0, Y1, Y2, and Y3 specimens with cylindrical steps.

Samples were cut off at the position of the $\Phi 6$ mm part of each specimen for electrochemical measurements. Before the electrochemical measurement, the samples were ground and polished, washed in ethanol, and dried in air. Electrochemical measurements were conducted using an electrochemical workstation (Corrtest instrument, CS150, Wuhan, China) having a conventional three-electrode system. A Hg/Hg₂SO₄ electrode was used as the reference electrode, a Pt plate electrode with an area of 20 mm $\times$ 20 mm was used as the counter electrode, and 1 mol/L Hg₂SO₄ solution was used as the corrosion solution. Before the electrochemical testing, the samples were exposed to the electrolyte until the open-circuit potential (OCP) became almost steady. Electrochemical-impedance-spectrum measurements (EIS) were performed in the frequency range from 10^5 Hz to 10^{-2} Hz at peak-to-peak sinusoidal voltage signals of 10 mV. Potentiodynamic polarization tests were conducted in a potential range from -0.3 V (vs. OCP) to 3 V with a potential sweep rate of 0.5 mV/s.

3. Results and Discussion

3.1. Structure Characterization

Figure 2 shows the XRD spectrum of the specimens, where obvious diffuse halos were observed around $30^\circ(2\theta)$ – $50^\circ(2\theta)$ in Y0, Y1, Y2, and Y3 specimens. The diffuse halos declare the existence of an amorphous phase in Y0, Y1, Y2, and Y3 specimens. The absence of crystalline-diffraction peaks indicates the fully amorphous nature of the Y2 and Y3 specimens. While for the XRD spectrum of Y0 and Y1 specimens, sharp peaks superimposed on the diffuse halos were observed. After indexing, these sharp peaks were found to correspond to the Al₅Ni₃Zr₂ intermetallic-compound phase and to the CuAlO₂ phase. The relative intensity of the feature peaks of the crystal phase in Y0 specimen was much higher than that of the Y1 specimen, indicating that the crystal-phase content in Y0 specimens was much higher than in Y1. Thus, according to the XRD spectrum, the crystalline phase gradually disappears with increasing yttrium doping content. The above results indicate that the Y1, Y2, and Y3 specimens possess greater GFA than Y0 specimens, and that proper yttrium doping content can enhance the GFA of the Zr_{50.7}Cu₂₈Ni₉Al_{12.3} MG.

It is noticed that the CuAlO₂ phase precipitates both in Y0 and Y1 specimens. The preferential formation of the CuAlO₂ phase indicates that one of the main inducements for the crystallization of the Zr_{50.7}Cu₂₈Ni₉Al_{12.3} specimens is the oxygen impurity in the melts. According to thermodynamic principles, yttrium has a stronger affinity for oxygen atom than zirconium [34,37]. Thus, by yttrium doping, the oxygen impurity can be scavenged via the formation of innocuous yttrium oxides of Y₂O₃. However, since the amount of the formed Y₂O₃ is still quite low in the alloy, no signal corresponding to Y₂O₃ phase appears in the XRD spectra.

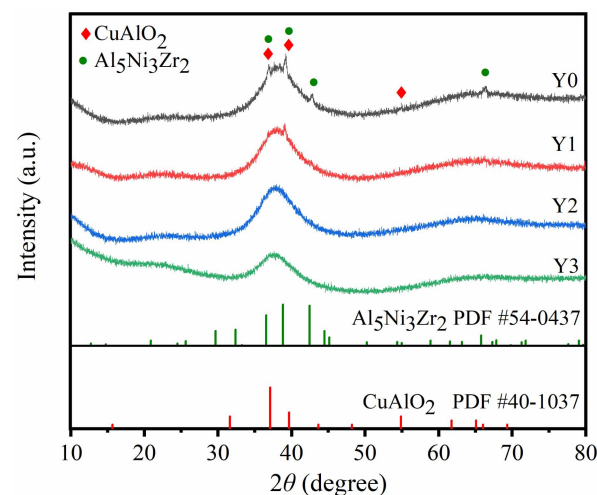


Figure 2. XRD spectra of the Y0, Y1, Y2 and Y3 specimens with $\phi 6$ mm.

3.2. Thermodynamic Parameters Characterization

Figure 3a shows the DSC curves of the Y0, Y1, Y2, and Y3 alloys. According to Figure 3a, the crystallization phenomenon can be clearly observed from the DSC curves. Figure S1 in the supplementary materials shows the enlarged DSC curves from 600 K to 800 K, where the glass-transition phenomenon can be clearly observed. According to the DSC curves, the glass transition temperature (T_g) and the onset-crystallization temperature (T_x) were indexed, and the results are listed in Table 1. It can be seen that the T_g and T_x keep decreasing with increasing yttrium doping content, as shown in Figure 4a,b. The high-temperature DSC curves of the Y0, Y1, Y2, and Y3 alloys were shown in Figure 3b. Onset melting temperature (T_m) and liquidus temperature (T_l) can be derived from the DSC curves, and the results are also shown in Table 1. It can be seen that the position and shape of the melting peaks are quite different for the four alloys. Thus, with different yttrium-doping content levels, the melting behavior and the microstructure of the $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ alloys significantly changes.

Table 1. The thermodynamic parameters of the Y0, Y1, Y2 and Y3 alloys.

Alloys	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT (K)	$T_{rg} (T_g/T_l)$	$\gamma (T_x/T_l + T_g)$	$\delta (T_x/T_l - T_g)$
Y0	737	784	1017	1143	47	0.645	0.417	1.931
Y1	727	780	1002	1137	53	0.639	0.418	1.902
Y2	722	779	1029	1116	57	0.647	0.424	1.977
Y3	709	767	1008	1112	58	0.638	0.421	1.903

Many parameters and indicators have been proposed to describe the GFA of alloys, such as $\Delta T_x (T_x - T_g)$ [38], $T_{rg} (T_g/T_l)$ [39], $\gamma (T_x/T_l + T_g)$ [40], $\delta (T_x/T_l - T_g)$ [41], $\beta (T_x/T_g + T_g/T_l)$ [42], and so on. Among the above parameters, the most-used parameters of ΔT_x , T_{rg} , γ and δ were selected to evaluate the GFA of the Y0–Y3 alloys. Commonly, larger values of these four parameters indicate greater GFA of the MG [39]. According to the thermodynamic parameters obtained from the DSC curves, the parameters were calculated and the results were listed in Table 1.

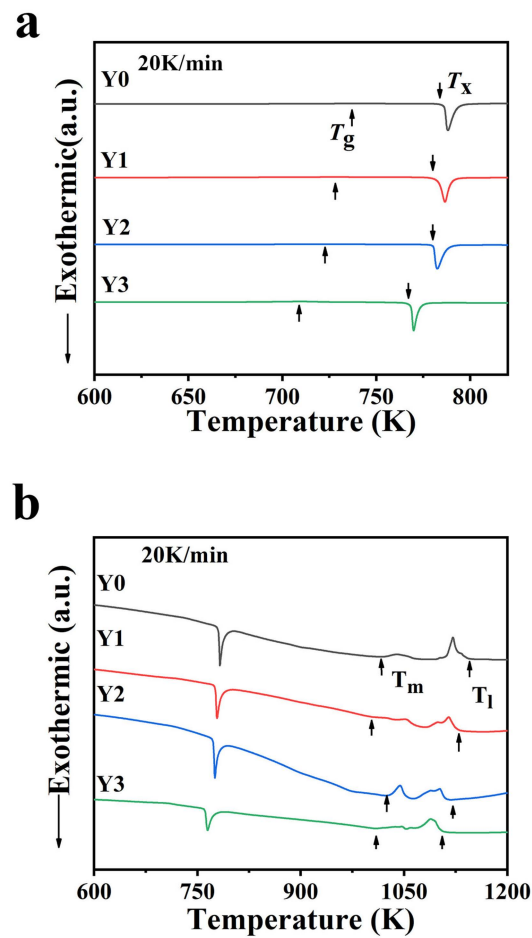


Figure 3. The (a) DSC and (b) high-temperature DSC curves of the Y0, Y1, Y2, and Y3 alloys.

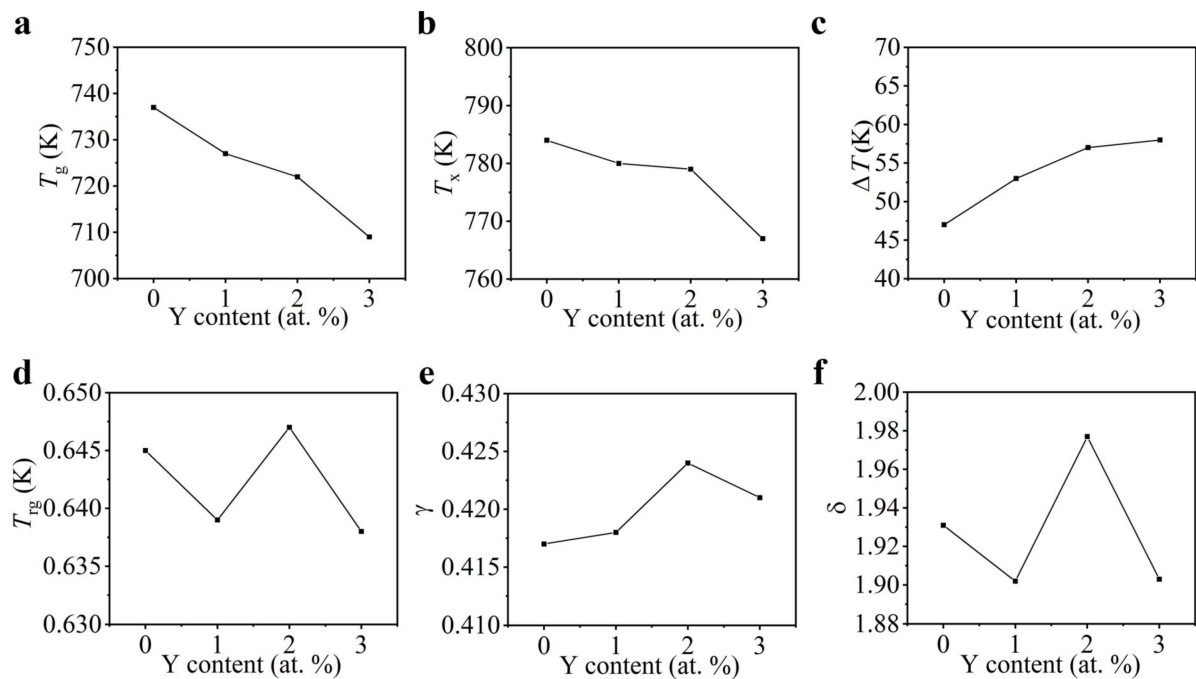


Figure 4. Plots of thermodynamic parameters vs. different yttrium doping contents of the Y0, Y1, Y2, and Y3 alloys: (a) T_g , (b) T_x , (c) ΔT , (d) T_{reg} , (e) γ , and (f) δ .

According to the data in Table 1, the relationship between the thermodynamic parameters and the yttrium-doping content of the $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ specimens is sorted out. It can be seen that the ΔT value increases with the content of yttrium doping, indicating that the doping of yttrium element can improve the super-cooled liquid thermal stability of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG. The T_{rg} values of Y1 and Y3 are both smaller than that of Y0, which is contradictory with the XRD results. The γ value first shows an increase and then a decreasing trend with increasing yttrium doping content. The minimum and maximum values of γ are obtained in the Y0 and Y2 specimen, respectively. The parameter δ exhibits a similar trend with T_{rg} , where Y2 possesses the maximum value among the yttrium doped alloys. Thus, considering the XRD results and the thermodynamic parameters of the $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ specimens, the Y2 alloy possesses the best GFA, and the parameter γ is most suitable for evaluating the GFA of the $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ alloy system.

It has been reported that the Zr-Cu-Ni-Al MGs are very sensitive to oxygen, and that crystallization is easy to occur due to the strong affinity of zirconium with oxygen [29]. Previous findings have shown that addition of a small amount of yttrium is effective in improving the GFA of Zr-based MGs, because the yttrium preferentially forms indifferent oxide better than zirconium [33–35,43]. However, over-doped yttrium will reduce the GFA-enhancement effect by increasing the in-situ crystallization tendency [35]. For example, Yan et al. found that the GFA of Zr-Cu-Ni-Al MG increases as the concentration of yttrium increases from 0 to 0.5 at. % and then decreases with further addition of yttrium content [35]. Thus, the proper doping of yttrium can increase the GFA of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG.

3.3. Activation Energy for Crystallization

Figure 5 shows the DSC curves of Y0, Y1, Y2, and Y3 alloys at different heating rates. The T_g , T_x and crystallization peak temperatures (T_p) were indexed from the DSC curves, and the results are listed in Table 2. It is obvious that T_g , T_x , and T_p shift to higher temperature with increasing heating rates, and that these phenomena are consistent with the previous reports [44].

Table 2. T_x and T_p values of the Y0, Y1, Y2 and Y3 alloys under different heating rates.

Alloys	Heating Rates (K/min)	T_g (K)	T_x (K)	T_p (K)
Y0	10	725	774	778
	20	737	784	788
	40	748	798	802
	60	761	808	812
Y1	10	719	771	776
	20	727	780	787
	40	741	796	800
	60	753	806	810
Y2	10	712	767	771
	20	722	779	782
	40	727	788	793
	60	737	798	802
Y3	10	699	759	761
	20	709	767	770
	40	719	777	780
	60	725	783	787

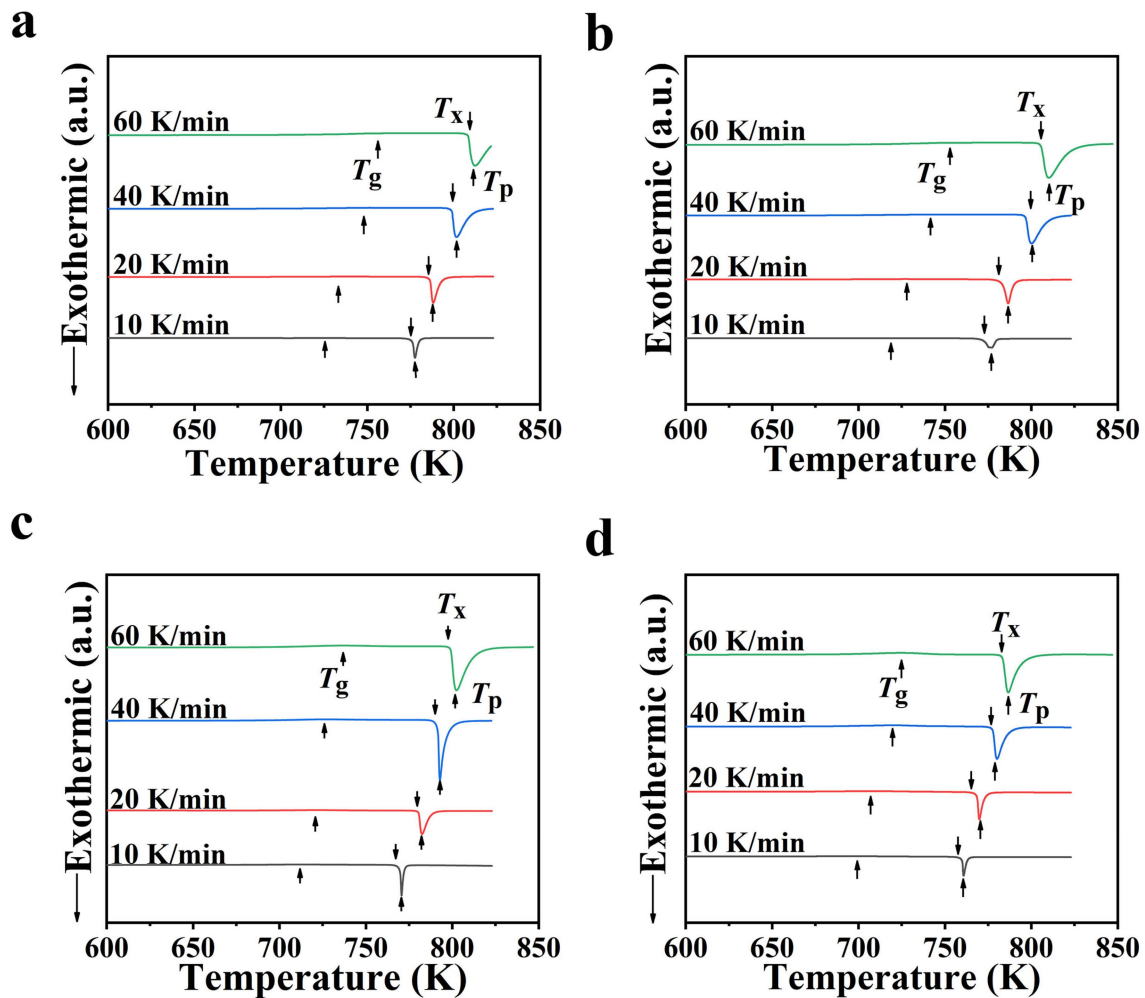


Figure 5. DSC curves of (a) Y0, (b) Y1, (c) Y2, and (d) Y3 alloys at various heating rates.

The effective activation energy for crystallization of the Y0, Y1, Y2, and Y3 alloys can be determined using the Kissinger equation [45]:

$$\ln\left(\frac{T^2}{\theta}\right) = \frac{E_c}{RT} + \ln\left(\frac{E_c}{k_0 R}\right) \quad (1)$$

where T is the specific temperature (T_x or T_p), θ is the heating rate, R is the gas constant, E_c is the activation energy, and k_0 is the frequency factor.

By substituting T_g , T_x , and T_p for T , respectively, the values-activation energy (i.e., E_g , E_x , and E_p) can be determined by the slope of a plot of the $\ln(T^2/\theta)$ against $1000/T$. The calculated results are plotted in Figure S2 in the supplementary materials, and the data are listed in Table 3. It can be seen that the Y2 alloy possesses the largest value of E_g . The value of E_x increases from 259 ± 19 kJ/mol to 349 ± 22 kJ/mol with yttrium doping. Thus, an increment of $\sim 35\%$ for E_x is achieved by the doping of yttrium. The value of E_p also increases from 261 ± 19 kJ/mol to 327 ± 19 kJ/mol, and an increment of $\sim 25\%$ is achieved.

To verify the results obtained using the Kissinger method, the effective activation energies for crystallization of the Y0, Y1, Y2, and Y3 alloys were also calculated by the Ozawa equation [44]:

$$\ln \theta = -1.0516 \frac{E_c}{RT} + C \quad (2)$$

The results calculated using Equation (2) are plotted in Figure S3 in the supplementary materials, and the data are listed in Table 3. As shown in Table 3, the activation energy calculated by the Ozawa equation is in accordance with that calculated by Kissinger

equation. Thus, the above results indicate the good reliability of the activation energies for crystallization calculated by the above two methods.

Table 3. Activation energy of the Y0, Y1, Y2 and Y3 alloys.

Alloys	Fitting Methods	E_g (kJ/mol)	E_x (kJ/mol)	E_p (kJ/mol)
Y0	Kissinger	221 ± 21	259 ± 19	261 ± 19
	Ozawa	222 ± 21	259 ± 18	261 ± 18
Y1	Kissinger	220 ± 28	244 ± 30	263 ± 15
	Ozawa	213 ± 27	258 ± 13	263 ± 14
Y2	Kissinger	312 ± 45	290 ± 22	288 ± 35
	Ozawa	308 ± 43	288 ± 20	286 ± 12
Y3	Kissinger	278 ± 1	349 ± 22	327 ± 19
	Ozawa	276 ± 1	348 ± 12	323 ± 18

Activation energy is an important parameter to characterize the thermodynamic stability of MGs. E_x represents the energy needed to overcome the crystallization barrier when atoms transition from disorder to order during the crystallization process [45]. E_p represents the energy required for the grain to grow [46]. Therefore, larger activation energy (E_g , E_x , and E_p) can indicate that the MG possesses higher resistance for crystallization to some extent. Figure 6 shows the change tendency of the E_g , E_x , and E_p of the $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ alloys with different amounts of yttrium doping. It can be seen that E_x and E_p present an increasing tendency with the doping of yttrium as a whole. This result indicates that more energy is needed for the nucleation and growth of grains after yttrium doping. Thus, the doping of yttrium can improve the resistance for crystallization of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG.

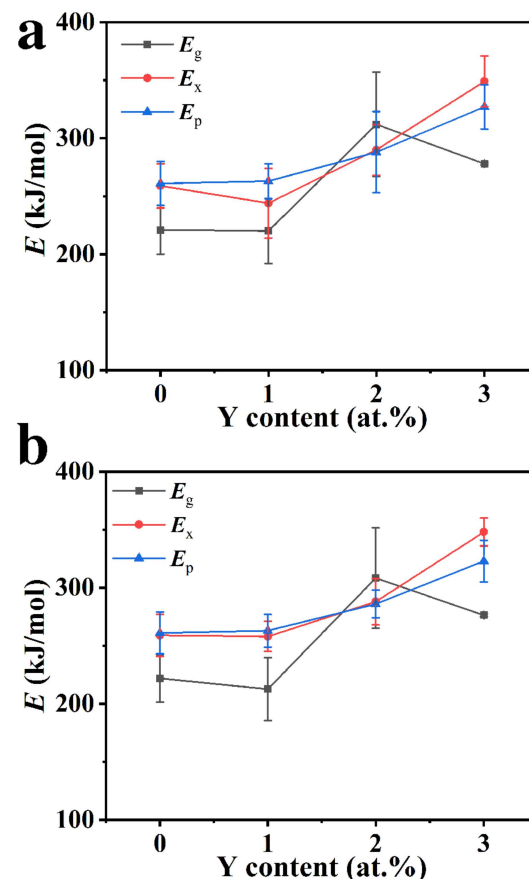


Figure 6. Plots of activation energies vs. different yttrium doping contents: (a) Kissinger fitting and (b) Ozawa fitting.

3.4. Corrosion Resistance Characterization

Figure 7a shows the potentiodynamic polarization curves of Y0, Y1, Y2, and Y3 specimens in a 1mol/L H_2SO_4 solution. Self-corrosion current density I_{corr} and self-corrosion potential E_{corr} are gained by fitting the curves using the Tafel extrapolation method. Generally, self-corrosion current density is proportional to the metal corrosion rate, and smaller self-corrosion current density indicates a lower corrosion rate as well as a higher resistant to corrosion [27]. The higher self-corrosion potential usually represents stronger corrosion resistance [16]. The fitting results are listed in Table 4 and plotted in Figure 8a,b. It can be seen that the self-corrosion potential significantly decreases after yttrium doping, and that the Y2 sample exhibits the highest self-corrosion potential among the yttrium doped samples. The doping of yttrium introduces a new element into the alloy. Due to the galvanic-cell effect, the newly introduced element will usually reduce the self-corrosion potential. Decrease of self-corrosion potential indicates that the occurrence of the corrosion becomes much easier after yttrium is doped into the alloy. The self-corrosion current density firstly decreases (Y0–Y2) and then increases with increasing yttrium doping content (Y2–Y3), and the Y2 alloy exhibits the lowest self-corrosion current density. Since the self-corrosion current density is closely related to the corrosion rate, the above results indicate that the Y2 alloy probably possesses the best corrosion resistance. The above results indicate that the Y2 samples possess the best corrosion resistance and that the Y3 samples possesses the worst corrosion resistance among the Y0, Y1, Y2, and Y3 samples.

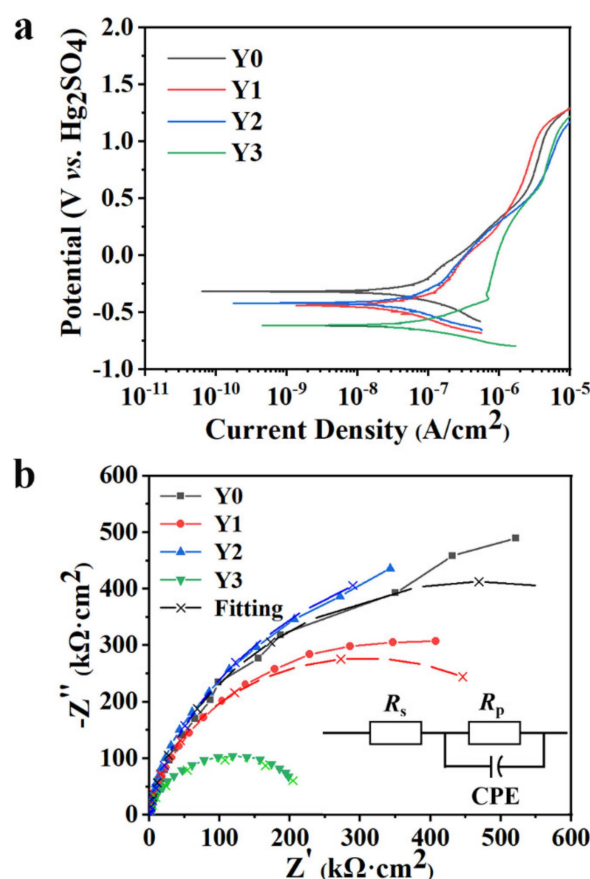
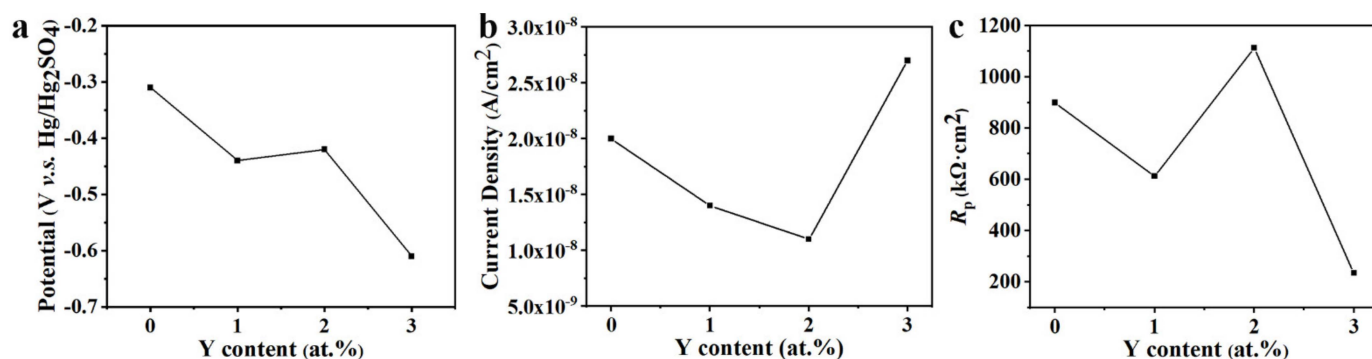


Figure 7. (a) Polarization curves and (b) Nyquist plots of the Y0, Y1, Y2, and Y3 samples with the equivalent circuit in the insert.

Table 4. Tafel fitting and EIS fitting results of the Y0, Y1, Y2 and Y3 samples.

Samples	E_{corr} (V)	I_{corr} (A/cm ²)	R_s ($\Omega \cdot \text{cm}^2$)	R_p (k $\Omega \cdot \text{cm}^2$)	CPE	
					n	Q_0 ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^{-n}$)
Y0	−0.31	2.0×10^{-8}	0.10	900	0.92	1.0×10^{-5}
Y1	−0.44	1.4×10^{-8}	0.04	613	0.94	1.3×10^{-5}
Y2	−0.42	1.1×10^{-8}	0.08	1114	0.90	2.0×10^{-5}
Y3	−0.61	2.7×10^{-8}	0.13	235	0.89	1.6×10^{-5}

**Figure 8.** (a) Plot of E_{corr} vs. yttrium doping content, (b) plot of I_{corr} vs. yttrium doping content, and (c) plot of R_p vs. yttrium doping content.

The decrease of self-corrosion current density from Y0 to Y2 may be caused by their different phase constitutions. As shown in Figure 2, a significant signal corresponding to crystal phase can be observed, indicating that obvious crystallization occurs. For the Y1 alloy, only a small peak corresponding to the crystalline phase can be observed, proving that there is a small amount of crystalline phase in the alloy. For the Y2 alloy, no obvious sharp peaks that correspond to crystalline phases can be observed, declaring its amorphous nature on the whole. According to Figure 2, it can be also found that the precipitated phase in Y0 and Y1 is a Cu-enriched phase (CuAlO_2). Our previous work had found that the Cu-enriched phase in the Zr-Cu-Ni-Al MG matrix composite (MGMC) is where pitting occurs [27]. The formation of the Cu-enriched phase will significantly reduce the corrosion resistance of the MGMC [24,27]. Thus, due to the decreasing content of Cu enriched phase (CuAlO_2), the self-corrosion current density decreases from Y0 to Y2. Y3 alloy also possesses an amorphous structure, as shown in Figure 2. Additionally, the above results of the thermodynamic parameters characterization show that the GFA of Y3 alloy is lower than that of the Y2 alloy. Thus, the yttrium is over-doped in Y3 alloy. According to the previous reports, over-doped yttrium will increase the in-situ crystallization tendency [35]. Since Cu-enriched phases tend to be preferentially precipitated in Zr-Cu-Ni-Al MGs [24,27], there may be many small clusters or nanocrystals of Cu enriched phase in the Y3 alloy. Thus, the self-corrosion current density of the Y3 alloy is much larger than the other alloys.

Figure 7b shows the Nyquist curve of the Y0, Y1, Y2, and Y3 samples in 1mol/L H_2SO_4 solution. The abscissa represents the real part of the impedance and the ordinate represents the imaginary part of the impedance. The R(CR) model was selected as the equivalent circuit, as shown in the insert of Figure 7b. The double-layer capacitance of passive film is described by a constant phase element (CPE). The value of CPE can be calculated by [47]:

$$Z(\text{CPE}) = Q_0^{\frac{1}{n}} \cdot R_p^{(1-\frac{1}{n})} \quad (3)$$

where Q_0 is the constant phase coefficient, R_p is the charge transfer resistance at the metal interface, and n is the dispersion index determined by surface heterogeneity ($0 \leq n \leq 1$). R_s is the solution resistance. Generally, R_p , which relates to morphology of the passive

film, can be used as an indicator of corrosion resistance [47]. A high R_p corresponds to the formation of a compact passive film, indicating that the migration of electrons through the solution interface is delayed [48]. A larger curvature radius indicates a higher impedance of the sample, and endows the sample with better corrosion resistance [16,49]. Based on the equivalent circuit diagram in Figure 7b, the Alternating Current (AC) impedance diagram was fitted using the Z view software, and the fitting results are shown in Table 4. It can be seen that the values of Q_0 and n of the Y0, Y1, Y2, and Y3 samples are very close, while the value of R_p exhibits significant difference. Figure 8c shows the plot of R_p vs. yttrium doping content. It can be seen that the Y2 sample has a maximum R_p value of $1.1 \times 10^7 \Omega \cdot \text{cm}^2$, and the Y3 sample has a minimum R_p value of $2.4 \times 10^6 \Omega \cdot \text{cm}^2$. Therefore, Y2 and Y3 have the best and the worst corrosion resistance, respectively. This result is consistent with the results obtained from the polarization curves.

According to the above results, it can be found that Y2 alloy possess the best GFA as well as the best corrosion resistance. Thus, the proper doping of yttrium can simultaneously increase the GFA, crystallization activation energy and corrosion resistance of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG. This work gives an important insight into the simultaneous increase of GFA, crystallization activation energy, and corrosion resistance of Zr-based MGs by element doping. Besides that, since Zr-Cu-Ni-Al MGs is a promising candidate for corrosion protective coatings [24,27], this work can greatly facilitate their final application.

4. Conclusions

$(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ ($x = 0, 1, 2, 3$) alloys were prepared by copper-mold casting. The effects of the yttrium-doping content on the GFA, crystallization activation energy, and corrosion resistance were studied. The following conclusions could be drawn from the study:

- (1) The yttrium doping can improve the GFA of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG. With increasing yttrium doping content, the GFA of the alloys firstly increases and then decreases. Y2 alloy possesses the best GFA among the $(\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3})_{100-x}\text{Y}_x$ ($x = 0, 1, 2, 3$) alloys.
- (2) The yttrium doping can improve the crystallization resistance of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG by increasing the activation energy for crystallization.
- (3) Compared to the Y0 alloy, the self-corrosion potential of the yttrium-doped MGs decreases, while the Y2 alloy's self-corrosion current density decreases and the charge transfer resistance at the metal interface significantly increases, indicating that the newly developed Y2 alloy exhibits enhanced corrosion resistance compared to the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG.
- (4) This work demonstrates the simultaneous increase of GFA, crystallization activation energy, and corrosion resistance of the $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ MG by proper yttrium doping. This can greatly facilitate the final application of Zr-Cu-Ni-Al MGs as protective coatings.

Supplementary Materials: The supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met13030521/s1>.

Author Contributions: Conceptualization, X.L.; Validation, Y.Q. and F.Q.; Investigation, Y.Z., L.Z., Y.Q. and L.H.; Resources, F.Q., L.Q., S.H. and X.L.; Data curation, Y.Q. and X.L.; Original draft preparation, Y.Z. and L.Z.; Review and editing, L.Q., S.H. and X.L.; Visualization, Y.Z. and Y.Q.; Supervision, L.Q. and X.L.; and Funding acquisition, F.Q., S.H. and X.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant Nos. 21908210, 51875539) and the Science and Technology on Surface Physics and Chemistry Laboratory Found (Grant No. WDZC202104).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Experimental data from this study are available from the corresponding author upon reasonable request.

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

References

- Halim, Q.; Mohamed, N.; Rejab, M.; Wan, N.; Ma, Q. Metallic glass properties, processing method and development perspective: A review. *Int. J. Adv. Manuf. Technol.* **2021**, *112*, 1231–1258. [\[CrossRef\]](#)
- Chen, Y.; Dai, Z.W.; Jiang, J.Z. High entropy metallic glasses: Glass formation, crystallization and properties. *J. Alloys Compd.* **2021**, *866*, 158852. [\[CrossRef\]](#)
- Liu, X.; Chen, N.; Gu, J.L.; Du, J.; Yao, K.F. Novel Cu-Ag bimetallic porous nanomembrane prepared from a multi-component metallic glass. *RSC Adv.* **2015**, *5*, 50565–50571. [\[CrossRef\]](#)
- Xie, S.; Zeng, X.; Qian, H. Correlations between the relaxed excess free volume and the plasticity in Zr-based bulk metallic glasses. *J. Alloys Compd.* **2009**, *480*, L37–L40. [\[CrossRef\]](#)
- Demetriou, M.D.; Launey, M.E.; Garrett, G.; Schramm, J.P.; Hofmann, D.C.; Johnson, W.L.; Ritchie, R.O. A damage-tolerant glass. *Nat. Mater.* **2011**, *10*, 123–128. [\[CrossRef\]](#)
- Liu, X.; Ma, B.; Hu, L.; Li, J.-F.; Qu, F.; Le, G.; Li, X. Fe-Si-Al Coatings with Stable Wear Resistance Prepared by Laser Cladding Industrial Wastes. *Metals* **2019**, *9*, 96. [\[CrossRef\]](#)
- Salehan, R.; Shahverdi, H.R.; Miresmaeili, R. Effects of annealing on the tribological behavior of Zr60Cu10Al15Ni15 bulk metallic glass. *J. Non-Cryst. Solids* **2019**, *517*, 127–136. [\[CrossRef\]](#)
- Khan, M.M.; Shabib, I.; Haider, W. A combinatorially developed Zr-Ti-Fe-Al metallic glass with outstanding corrosion resistance for implantable medical devices. *Scr. Mater.* **2019**, *162*, 223–229. [\[CrossRef\]](#)
- Zhang, G.; Sun, W.; Xie, L.; Zhang, C.; Tan, J.; Peng, X.; Li, Q.; Ma, X.; Zhao, D.; Yu, J. Multicomponent Fe-Based Bulk Metallic Glasses with Excellent Corrosion and Wear Resistances. *Metals* **2022**, *12*, 564. [\[CrossRef\]](#)
- Yu, M.; Zhang, M.; Sun, J.; Liu, F.; Wang, Y.; Ding, G.; Xie, X.; Liu, L.; Zhao, X.; Li, H. Facile Electrochemical Method for the Fabrication of Stable Corrosion-Resistant Superhydrophobic Surfaces on Zr-Based Bulk Metallic Glasses. *Molecules* **2021**, *26*, 1558. [\[CrossRef\]](#)
- Liu, X.; Gu, J.-L.; Yang, G.-N.; Shao, Y.; Chen, N.; Yao, K.-F. Theoretical and experimental study of metallic glass die-imprinting for manufacturing large-size micro/nano structures. *J. Mater. Process. Technol.* **2022**, *307*, 117699. [\[CrossRef\]](#)
- Liu, X.; Shao, Y.; Han, Z.D.; Yao, K.F. Morphology and structure evolution of metallic nanowire arrays prepared by die nanoimprinting. *Sci. Bull.* **2015**, *60*, 629–633. [\[CrossRef\]](#)
- Kumar, G.; Tang, H.X.; Schroers, J. Nanomoulding with amorphous metals. *Nature* **2009**, *457*, 868–872. [\[CrossRef\]](#)
- Souza, C.A.C.; Ribeiro, D.V.; Kiminami, C.S. Corrosion resistance of Fe-Cr-based amorphous alloys: An overview. *J. Non-Cryst. Solids* **2016**, *442*, 56–66. [\[CrossRef\]](#)
- Yang, X.; Gao, M.; Liu, Y.; Li, J.; Huang, Y.; Wang, G.; Wang, J.-Q.; Huo, J. Superior corrosion resistance of high-temperature Ir-Ni-Ta-(B) amorphous alloy in sulfuric acid solution. *Corros. Sci.* **2022**, *200*, 110227. [\[CrossRef\]](#)
- Yang, Y.J.; Fan, X.D.; Wang, F.L.; Qi, H.N.; Yue, Y.; Ma, M.Z.; Zhang, X.Y.; Li, G.; Liu, R.P. Effect of Nb content on corrosion behavior of Ti-based bulk metallic glass composites in different solutions. *Appl. Surf. Sci.* **2019**, *471*, 108–117. [\[CrossRef\]](#)
- Baulin, O.; Bugnet, M.; Fabrègue, D.; Lenain, A.; Gravier, S.; Cazottes, S.; Kapelski, G.; Ter-Ovanesian, B.; Balvay, S.; Hartmann, D.J.; et al. Improvement of mechanical, thermal, and corrosion properties of Ni- and Al-free Cu-Zr-Ti metallic glass with yttrium addition. *Materialia* **2018**, *1*, 249–257. [\[CrossRef\]](#)
- Yao, K.F.; Kui, H.W. Evidence of a two-dimensional nucleation and growth mechanism for metastable nanocrystals embedded in Pd40.5Ni40.5P19 glass. *Appl. Phys. Lett.* **2000**, *77*, 2313–2315. [\[CrossRef\]](#)
- Gong, P.; Wang, X.; Shao, Y.; Chen, N.; Liu, X.; Yao, K.F. A Ti-Zr-Be-Fe-Cu bulk metallic glass with superior glass-forming ability and high specific strength. *Intermetallics* **2013**, *43*, 177–181. [\[CrossRef\]](#)
- 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. [\[CrossRef\]](#)
- Li, J.F.; Shao, Y.; Liu, X.; Yao, K.F. Fe-based bulk amorphous alloys with high glass formation ability and high saturation magnetization. *Sci. Bull.* **2015**, *60*, 396–399. [\[CrossRef\]](#)
- Liu, X.; Shao, Y.; Lu, S.Y.; Yao, K.F. High-accuracy bulk metallic glass mold insert for hot embossing of complex polymer optical devices. *J. Polym. Sci. Part B Polym. Phys.* **2015**, *53*, 463–467. [\[CrossRef\]](#)
- Gulenko, A.; Chungong, L.F.; Gao, J.; Todd, I.; Hannon, A.C.; Martin, R.A.; Christie, J.K. Atomic structure of Mg-based metallic glasses from molecular dynamics and neutron diffraction. *Phys. Chem. Chem. Phys.* **2017**, *19*, 8504–8515. [\[CrossRef\]](#) [\[PubMed\]](#)
- Hu, L.; Liu, X.; Chen, T.; Le, G.; Li, J.; Qu, F.; Zhou, Y.; Qi, L.; Wang, D. Characterization of laser clad Zr-Cu-Ni-Al in-situ metallic glass matrix composite coatings with enhanced corrosion-resistance. *Vacuum* **2021**, *185*, 109996. [\[CrossRef\]](#)
- Lu, S.; Li, X.; Liang, X.; He, J.; Shao, W.; Li, K.; Chen, J. Effect of Ho Addition on the Glass-Forming Ability and Crystallization Behaviors of Zr54Cu29Al10Ni7 Bulk Metallic Glass. *Materials* **2022**, *15*, 2516. [\[CrossRef\]](#)
- Huang, C.H.; Huang, J.C.; Li, J.B.; Jang, J.S.C. Simulated body fluid electrochemical response of Zr-based metallic glasses with different degrees of crystallization. *Mater. Sci. Eng. C* **2013**, *33*, 4183–4187. [\[CrossRef\]](#)

27. Hu, L.; Liu, X.; Liang, C.; Zhao, S.; Chen, T.; Li, J.; Le, G.; Qu, F.; Zhou, Y.; Qi, L.; et al. Microstructure evolution and corrosion mechanism of laser cladded Zr-Cu-Ni-Al in-situ metallic glass matrix composite coatings. *Surf. Coat. Technol.* **2021**, *409*, 126908. [\[CrossRef\]](#)
28. Zhou, W.; Meng, Y.; Duan, F.; Huang, W.; Yao, J.; Pan, J.; Wang, Y.; Li, Y. The effect of oxygen on phase formation in an industrial Zr based bulk metallic glass. *Intermetallics* **2021**, *129*, 107055. [\[CrossRef\]](#)
29. Eckert, J.; Mattern, N.; Zinkevitch, M.; Seidel, M. Crystallization behavior and phase formation in Zr-Al-Cu-Ni metallic glass containing oxygen. *Mater. Trans. JIM* **1998**, *39*, 623–632. [\[CrossRef\]](#)
30. Gebert, A.; Eckert, J.; Schultz, L. Effect of oxygen on phase formation and thermal stability of slowly cooled Zr₆₅Al₁₇. 5Cu₁₇. 5Ni₁₀ metallic glass. *Acta Mater.* **1998**, *46*, 5475–5482. [\[CrossRef\]](#)
31. Luo, J.; Duan, H.; Ma, C.; Pang, S.; Zhang, T. Effects of yttrium and erbium additions on glass-forming ability and mechanical properties of bulk glassy Zr-Al-Ni-Cu alloys. *Mater. Trans.* **2006**, *47*, 450–453. [\[CrossRef\]](#)
32. Hu, Q.; Fu, M.; Zeng, X. Thermostability and thermoplastic formability of (Zr₆₅Cu₁₇. 5Ni₁₀Al₁₇. 5)_{100-x}RE_x (x = 0.25–3.25, RE: Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) bulk metallic glasses. *Mater. Des.* **2014**, *64*, 301–306. [\[CrossRef\]](#)
33. Yan, M.; Shen, J.; Zhang, T.; Zou, J. Enhanced glass-forming ability of a Zr-based bulk metallic glass with yttrium doping. *J. Non-Cryst. Solids* **2006**, *352*, 3109–3112. [\[CrossRef\]](#)
34. Hao, G.J.; Zhang, Y.; Lin, J.P. Bulk metallic glass formation of Ti-based alloys from low purity elements. *Mater. Lett.* **2006**, *60*, 1256–1260. [\[CrossRef\]](#)
35. Yan, M.; Zou, J.; Shen, J. Effect of over-doped yttrium on the microstructure, mechanical properties and thermal properties of a Zr-based metallic glass. *Acta Mater.* **2006**, *54*, 3627–3635. [\[CrossRef\]](#)
36. Sun, Y.J.; Qu, D.D.; Huang, Y.J.; Liss, K.D.; Wei, X.S.; Xing, D.W.; Shen, J. Zr-Cu-Ni-Al bulk metallic glasses with superhigh glass-forming ability. *Acta Mater.* **2009**, *57*, 1290–1299. [\[CrossRef\]](#)
37. Baulin, O.; Douillard, T.; Fabrègue, D.; Perez, M.; Pelletier, J.-M.; Bugnet, M. Three-dimensional structure and formation mechanisms of Y₂O₃ hollow-precipitates in a Cu-based metallic glass. *Mater. Des.* **2019**, *168*, 107660. [\[CrossRef\]](#)
38. Nishiyama, N.; Inoue, A. Direct comparison between critical cooling rate and some quantitative parameters for evaluation of glass-forming ability in Pd-Cu-Ni-P alloys. *Mater. Trans.* **2002**, *43*, 1913–1917. [\[CrossRef\]](#)
39. Inoue, A. Stabilization of metallic supercooled liquid and bulk amorphous alloys. *Acta Mater.* **2000**, *48*, 279–306. [\[CrossRef\]](#)
40. Lu, Z.; Liu, C. A new glass-forming ability criterion for bulk metallic glasses. *Acta Mater.* **2002**, *50*, 3501–3512. [\[CrossRef\]](#)
41. Chen, Q.; Shen, J.; Zhang, D.; Fan, H.; Sun, J.; McCartney, D. A new criterion for evaluating the glass-forming ability of bulk metallic glasses. *Mater. Sci. Eng. A* **2006**, *433*, 155–160. [\[CrossRef\]](#)
42. Mondal, K.; Murty, B. On the parameters to assess the glass forming ability of liquids. *J. Non-Cryst. Solids* **2005**, *351*, 1366–1371. [\[CrossRef\]](#)
43. Chen, J.; Zhang, Y.; He, J.P.; Yao, K.F.; Chen, G.L. Metallographic analysis of Cu-Zr-Al bulk amorphous alloys with yttrium addition. *Scr. Mater.* **2006**, *54*, 1351–1355. [\[CrossRef\]](#)
44. Luo, Y.; Ke, H.; Zeng, R.; Liu, X.; Luo, J.; Zhang, P. Crystallization behavior of Zr₆₀Cu₂₀Fe₁₀Al₁₀ amorphous alloy. *J. Non-Cryst. Solids* **2020**, *528*, 119728. [\[CrossRef\]](#)
45. Yang, Y.; Cheng, B.; Jin, Z.; Gao, H.; Ma, M.; Zhang, X. Crystallization kinetics and mechanical properties of Zr₅₆Cu₂₄Al₉Ni_{7-x}Ti₄Ag_x (x = 0, 1, 3, 5, and 7) metallic glasses. *J. Alloys Compd.* **2020**, *816*, 152589. [\[CrossRef\]](#)
46. Bizhanova, G.; Li, F.; Ma, Y.; Gong, P.; Wang, X. Development and crystallization kinetics of novel near-equiatomic high-entropy bulk metallic glasses. *J. Alloys Compd.* **2019**, *779*, 474–486. [\[CrossRef\]](#)
47. Xu, K.; Lan, A.; Qiao, J.; Yang, H.; Han, P.; Liaw, P. Corrosion behaviors and mechanisms of in-situ Ti-based MGMCs in chloride-containing and chloride-free solutions. *Intermetallics* **2019**, *105*, 179–186. [\[CrossRef\]](#)
48. Wang, X.; Gao, Y.; Li, K.; Yan, J.; Li, Y.; Feng, J. Effect of yttrium on the corrosion behaviour of 09CrCuSb alloy in concentrated sulphuric acid. *Corros. Sci.* **2013**, *69*, 369–375. [\[CrossRef\]](#)
49. Yu, L.; Tang, J.; Wang, H.; Wang, Y.; Qiao, J.; Apreutesei, M.; Normand, B. Corrosion behavior of bulk (Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀)_{100-x}Y_x (x = 0, 0.5, 2.5 at.%) metallic glasses in sulfuric acid. *Corros. Sci.* **2019**, *150*, 42–53. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.