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REVIEW
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A Brief Introduction on the Development of Ti-Based Metallic Glasses

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Ti-based metallic glasses (MGs) possess high specific strength, low elastic modulus, high elasticity, high wear and corrosion resistance, and excellent biocompatibility, which make them highly attractive as lightweight high-strength materials as well as biomaterials. However, the glass forming ability (GFA) of Ti-based MGs, particularly those bearing no toxic, noble, or heavy metals, that is, Be, Pd, or Cu alike, largely sets back their wide applications for the restricted critical glass forming size of these Ti-based MGs. In this review, the outlines in developing Ti-based MGs are delineated in order to provide an overall view on the efforts ever made to fabricate bulk size Ti-based MGs. The state of the art in the knowledge on the GFA of Ti-based MGs is briefly introduced, and possible directions for fabricating bulk size toxic and noble element free Ti-based MGs are discussed.

Keywords: Ti-based metallic glasses, glass forming ability, biomaterials, lightweight high-strength materials, composition design

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BACKGROUND

The disordered atomic packing in metallic glasses (MGs) makes them drastically different from conventional crystalline alloys and exhibit novel physical, chemical, and mechanical properties (Wang et al., 2004; Wang, 2009; Zhang et al., 2019). For the high specific strength, corrosion resistance, and biocompatibility of Ti element, Ti-based MGs have been attracting intensive attentions for their potential applications as lightweight high-strength materials (Jiang et al., 2015) and biomaterials (Li and Zheng, 2016). Early observations of non-crystalline phases in titanium alloys were made in binary TiCu and TiNi alloys in the late 1960s *via* splat quenching (Polk et al., 1978), for the large difference in atomic size between early transition metals (Ti) and late transition metals (Cu, Ni). Later on, lightweight Ti-based MG with a nominal composition of $Ti_{50}Be_{40}Zr_{10}$ (i.e., METGLAS 2204) was first reported by Tanner and Ray in 1977 in the TiBeZr ternary system (Tanner and Ray, 1977). To date, hundreds of Ti-based MGs have been found (Gong et al., 2016) with improved glass forming ability (GFA) and intriguing mechanical and chemical properties, which effectively support the application of Ti-based MGs. The GFA of MGs generally refers to the lowest cooling rate required for the undercooled liquid to bypass crystallization and become a glass and is conveniently measured with the critical size of an MG sample (often the diameter of a rod) that could be cast into a fully amorphous state. However, those Ti-based MGs with excellent GFA (i.e., large critical diameter) (Gong et al., 2016) usually contain toxic element—Be, noble metal—Pd, or heavy late transition metals—Cu or Ni. The presence of these elements, to a certain extent, impairs the application prospects of Ti-based MGs. To summarize the achievements ever made and illuminate the directions for future research, the main development paths of Ti-based

MGs are sorted out in this review. Based on the development paths of Ti-based MGs, 4 series of Ti-based MGs could be categorized according to the main composing elements, that is, TiCuNi series MGs, TiZrBe series MGs, TiZrCu series MGs, and TiZrSi series MGs.

In the following part, the successful preparation of each series of Ti-based MGs will be introduced in more detail, respectively. Here, we would like to emphasize that this review focuses mainly on the history of the observation of Ti-based MGs and the effect of alloying elements on the critical diameter of Ti-based MGs. Statistical data on the criteria of GFA for Ti-based MGs, such as the width of the supercooled liquid region $\Delta T_x = T_x - T_g$, the reduced glass transition temperature $T_{rg} = T_g/T_l$, and the parameter $\gamma = T_x/(T_g + T_l)$, are not focused on, where T_g is the glass transition temperature, T_x is the crystallization temperature, and T_l is the liquidus temperature. Moreover, the mechanical, physical, and chemical properties of Ti-based MGs are not encompassed either. For details on these aspects of Ti-based MGs, the readers are referred to more comprehensive reviews (Jiang et al., 2015; Gong et al., 2016; Li and Zheng, 2016). In the end, based on a global view on the development of Ti-based MGs, potential routes are discussed for the fabrication of new toxic and noble element free Ti-based MGs with bulk size.

DEVELOPMENT PATHS OF TI-BASED MGS

TiCuNi Series

In early days, glass formation and their structures of Ti-based MGs were mainly focused on to recognize these new glass materials. For example, early research studies on Ti (Cu, Fe) binary MGs were made based on their hydrogen absorption behaviors (Maeland et al., 1978; Rodmacq et al., 1988). Crystallization kinetics in amorphous TiCu and TiNi binary systems were examined by Buschow in 1983 (Buschow, 1983a; Buschow, 1983b) and in TiPt by Gao and Wang (Yi Qun Gao and Whang, 1985) in 1985, and later on, those of $Ti_{74.8}Ni_{13.1}Cu_{12.1}$, $Ti_{50}Ni_5Cu_{45}$, $Ti_{70.8}Ni_{13.3}Cu_{12.3}Ge_{3.6}$, and $Ti_{66.6}Cu_{12.5}Ni_{13.6}Ge_{7.3}$ MGs were also analyzed (Šušić et al., 1986; Gao et al., 1989). Chemical short range orders in TiNi MGs (Fukunaga et al., 1983; Fukunaga et al., 1984) were found to be analogous to that in corresponding crystalline compounds. Coexistence of two glass phases was observed in $Ti_{61}Cu_{23}Ni_{16}$ and $Ti_{62.5}Cu_{12}Ni_{23}Si_{2.5}$ MGs (Duhaj et al., 1985). Electronic configurations in TiCu, TiCuAl, and TiCuSi MGs (Tanaka et al., 1988) were studied by Tanaka *et al.*, and the results suggested that the chemical affinity of elements Si and Al for late and early transition metals is highly relevant to the GFA of these MGs.

Studies engaging in enhancing the GFA of Ti-based MGs rapidly emerged in the 1990s. Glass forming compositions in the ternary TiCuNi system with a wide supercooled liquid region (SLR) were reported in 1994 (Zhang et al., 1994). It was found that the glass forming composition range in the TiCuNi ternary system was with Ni from 0 to 50 at% and Cu from 0 to 75 at%, in which the $Ti_{50}Ni_{25}Cu_{25}$ MG showed the widest SLR of 55 K. Since a wide SLR indicates high thermal stability of supercooled liquid and possibly good GFA (Inoue, 2000), great efforts were

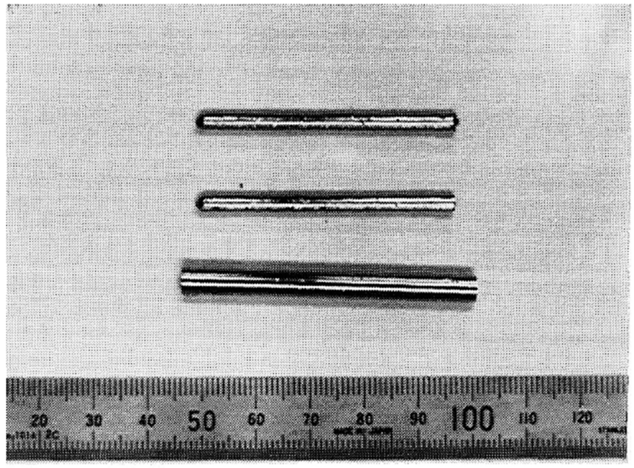

FIGURE 1 | $Ti_{50}Cu_{25}Ni_{15}Sn_5Zr_5$ MG rods of 3 and 6 mm diameter (from Zhang *et al.* (Zhang and Inoue, 1998)).

dedicated to the search for compositions with wider SLR. $Ti_{65}Ni_{25}Al_{10}$ and $Ti_{65}Cu_{25}Al_{10}$ MGs were also examined but to show no clear glass transition phenomenon before setting in of crystallization (Zhang et al., 1993). To widen the SLR of Ti-based MGs, different ternary systems Ti-Cu-(Ni, Co, Fe, and Si) were tried out (Inoue et al., 1994), whereas a quaternary $Ti_{50}Cu_{25}Ni_{20}Co_5$ MG was found to show an SLR of 90 K, but the GFA remained marginal. In 1998, the effects of Sn (and Zr) and Sb on the thermal stability of the ternary $Ti_{50}Cu_{25}Ni_{20}$ system were examined (Zhang and Inoue, 1998). With 5 at% replacement of Ni by Sn, $Ti_{50}Cu_{25}Ni_{20}Sn_5$ MG showed an SLR of 60 K. The authors argued that the similar size of Sn (atomic radius 0.141 nm) to Ti (0.147 nm) enabled Sn to replace Ti in its compounds and the replacement of Sn to Ti altered the crystallization mode and stabilized the supercooled liquid. However, with 3 at% replacement of Ni by Sb also of a similar size (0.145 nm) to Ti, the SLR was reduced to 45 K for unclear reasons. Intriguingly, as shown in **Figure 1**, it was also found that by further alloying with Zr, the $Ti_{50}Cu_{25}Ni_{15}Sn_5Zr_5$ MG showed a critical glass forming size of 6 mm rod diameter, indicating the crucial role of Zr in GFA. With slight composition variation, a $Ti_{50}Cu_{32}Ni_{15}Sn_3$ MG was found to show an SLR of 73 K and a critical diameter of 1 mm (Kim et al., 2001), suggesting the positive effect of Sn on GFA. In the meantime, for the smaller atomic sizes, metalloid elements Si (0.117 nm) and B (0.09 nm) were introduced to fabricate $Ti_{50}Cu_{20}Ni_{24}Sn_3B_1Si_2$ and $Ti_{50}Cu_{20}Ni_{24}B_2Si_4$ MGs (Zhang and Inoue, 1999; Zhang and Inoue, 2001) with SLRs of 74 and 65 K in width, respectively. $Ti_{50}Cu_{20}Ni_{24}Sn_3B_1Si_2$ MG could also be cast into rods of a diameter of 1 mm. The authors believed that this was because the addition of B and Si enabled the 2 MGs to satisfy the 3 empirical rules of Inoue (Inoue, 2000) for glass formation, that is, (1) multicomponent with more than 3 main elements, 2) significant differences in atomic size above 12% of main elements, and 3) negative mixing heats among main elements.

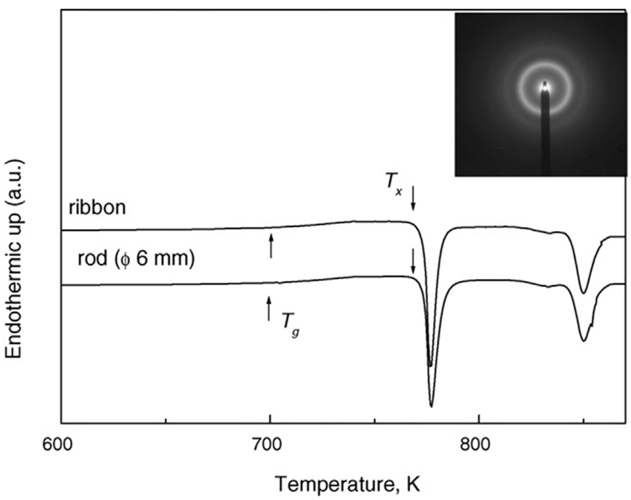

FIGURE 2 | Thermograms for $Ti_{41.5}Zr_{2.5}Hf_5Cu_{37.5}Ni_{7.5}Si_1Sn_5$ MG ribbon and rod (6 mm). The inset shows the SAED pattern of the rod of 6 mm diameter (from Huang et al. (2007)).

In 2002, based on $Ti_{50}Cu_{32}Ni_{15}Sn_3$ MG, Kim et al. (2002), by replacing Cu (0.128 nm) with Be (0.113 nm) which is of smaller size and has larger mixing heat with Ti, prepared the $Ti_{50}Cu_{25}Ni_{15}Sn_3Be_7$ MG with a critical diameter of 2 mm. The effects of Zr, Mo, and Ta on the glass formation of TiCuNiSn system were examined by He et al. (2003); He et al. (2004a); He et al. (2004b); He et al. (2006). However, mainly, amorphous ribbons could be fabricated. This was because the addition of Zr, Mo, and Ta lower the GFA by extending the melting interval and introducing nucleation sites for β-Ti solid solutions. Following Inoue's rule, Kim et al. (2003); Kim et al. (2004); Park et al. (2004); Kim et al. (2007) further proposed to add Be and Zr into the quaternary TiCuNiSn system, and $Ti_{45}Cu_{25}Ni_{15}Sn_3Be_7Zr_5$ and $Ti_{40}Ni_8Cu_9Be_{18}Zr_{25}$ MGs of critical diameters of 5 and 8 mm, but smaller SLR widths of 61 and 47 K were prepared. For the high content of Be and Zr, $Ti_{40}Ni_8Cu_9Be_{18}Zr_{25}$ MG actually enters the TiZrBe series and suggests the potential high GFA of TiZrBe series MGs. It also seems that GFA does not agree well with the width of SLR, indicating the decoupling between GFA and thermal stability of undercooled liquid.

Similar to previous studies, in 2004, Ma et al. (2004a) examined the effect of Zr, Hf, and Si on the GFA of $Ti_{50}Cu_{42.5}Ni_{7.5}$ MG and found that $Ti_{41.5}Cu_{42.5}Ni_{7.5}Zr_{2.5}Hf_5Si_1$ MG exhibits a critical diameter of 5 mm. The increased GFA was mainly because the addition of Zr moved the composition closer to the eutectic "valley" (lower liquid temperature and possibly higher T_{rg} prone to glass formation) and the addition of Si stabilized the supercooled liquid, leading to the formation of local atomic structures. They (Ma et al., 2004b) also examined the effects of B, Al, and Zr on the glass formation in the TiCuNiSi system and reported $Ti_{53}Cu_{15}Ni_{18}Al_7Zr_3Si_3B_1$ MG and $Ti_{53}Cu_{15}Ni_{18.5}Al_7Zr_3Si_3B_{0.5}$ MG with a critical diameter of 2.5 mm. They found that small atom B was important in enhancing GFA for interactions with other elements and more efficient packing mode. Sun *et al.* also characterized the effect of small atom C (0.077 nm) on the GFA of $Ti_{50}Cu_{23}Ni_{20}Sn_7$ MG (Sun et al., 2005) but fabricated only MG composites. Later then, according to the topological glass formation model (Egami et al., 2007), early transition metals M (= Hf (0.160 nm), Zr (0.162 nm), and Sc (0.165 nm)) with large atomic sizes were introduced into $Ti_{53}Cu_{15}Ni_{18.5}Al_7Si_3B_{0.5}M_3$ (Xia et al., 2005a; Xia et al., 2005b; Xia et al., 2005c; Xia et al., 2005d) to prepare new Ti-based BMGs with critical diameters of 2.5 mm, indicating no prominent effect of Hf and Sc on GFA. In 2007, based on Ma *et al.*'s work (Ma et al., 2004a). Huang et al. (2007) found that $Ti_{41.5}Cu_{37.5}Ni_{7.5}Zr_{2.5}Hf_5Si_1Sn_5$ MG showed the best ever GFA in TiCuNi series MGs with a critical diameter of 6 mm, as shown in **Figure 2**, indicating the enhancement of GFA by Sn addition. Interestingly, with an equal atomic ratio, thst is, assisted by the high entropy effect (Greer, 1993) and the coexistence of Ti, Zr, and Be, TiCuNiZrHfBe MG shows a much increased critical diameter of 15 mm (Gong et al., 2015). However, TiNi (Al, Si, and Sn) ternary systems were re-examined to show limited GFA (Lu and Xu, 2008; Lu et al., 2009a; Lu et al., 2009b). By "3D pinpointing approach," Wang *et al.* (Wang and Xu, 2008) found a series of quaternary (Ti, Zr) CuNi MGs with a critical diameter of 3 mm and proposed that the substitution of Zr for Ti increased GFA for its atomic size difference with Ti and negative mixing heat with Ni and Cu. Recently, Chen and Hsu also examined the effect of Sn on the GFA of a $Ti_{44}Cu_{40}Ni_{16}$ alloy and reported a best glass former of $Ti_{44}Cu_{40}Ni_{16}Sn_1$ (Chen and Hsu, 2016) with a critical diameter of around 4 mm.

The development of TiCuNi series MGs was aimed at increasing the GFA and enlarging the SLR, that is, alloying with elements of large atomic size ratios, and attractive bonding nature to increase the difficulty in the redistribution of constituent elements for crystallization. This principle later developed into the 3 rules of Inoue. To enhance the GFA, C, Si, Sn, Sb, B, Zr, Hf, Sc, Be, Fe, Mo, Al, and Ta have been added into the TiCuNi system separately. The elements playing a positive role could be identified as Sn, Zr, Be, B, Si, and Hf. More importantly, as summarized before, coexistence of 2 or more elements would be crucial in enhancing the GFA of TiCuNi series MGs, for example, Zr + Sn (Zhang and Inoue, 1998; Wang and Xu, 2008), Zr + Be (Kim et al., 2003; Kim et al., 2004; Park et al., 2004; Kim et al., 2007), and Zr + Si (Ma et al., 2004a). This fact is worthy of further investigation for improving the GFA. However, the GFA of TiCuNi series MGs remains way small when compared to Zr-based (73 mm) (Lou et al., 2011) and Pd-based (85 mm) MGs (Nishiyama et al., 2012). On the other hand, the large amount of Cu and Ni largely lowers the specific strength of Ti-based MGs. To this situation, the TiZrBe series MGs with high GFA and lower density were rapidly developed in the past decades.

TiZrBe Series

The fabrication of TiZrBe series MGs dates back to the synthesis of METGLAS 2204 (Tanner and Ray, 1977) by Tanner and Ray with high specific strength and a stable enough supercooled liquid state for the preparation of continuous ribbon. MG formation in binary TiBe and ZrBe systems was reported later in 1979, and it was found that glass formation compositions were near the

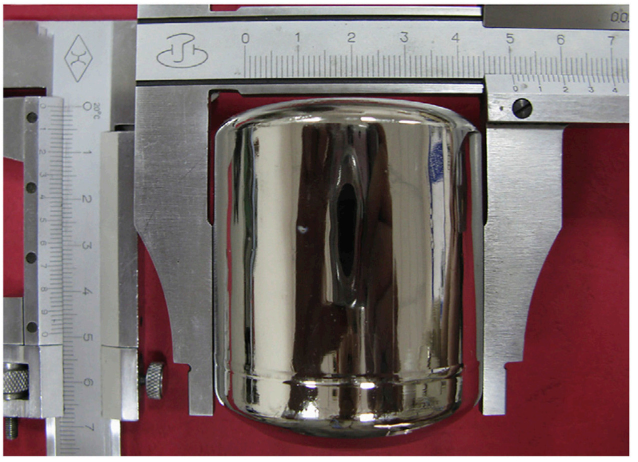

FIGURE 3 | $Ti_{32.8}Zr_{30.2}Cu_9Fe_{5.3}Be_{22.7}$ MG rod with a diameter of 50 mm (from Zhang et al. (2015)).

eutectic point and that ZrBe exhibited better GFA than TiBe (Tanner and Ray, 1979). The formation of TiBe (Si, Al) (Tanner, 1978; Tanner et al., 1988) MGs and phase separation in the TiZrBe (Tanner and Ray, 1980) system were also studied. In 1993, with the preparation of Vitreloy 1 ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ MG) (Peker and Johnson, 1993), the first commercialized bulk metallic glass (BMG, referring to metallic glass that could be cast into a sample of over 1 mm in all 3 dimensions), the TiZrBe series MGs were under intensive study for bulk specimen forming compositions.

In 2002, for the small atomic size (0.113 nm) and negative mixing heat (−30 k J/mol) with Ti, Be was used in making $Ti_{50}Cu_{25}Ni_{15}Sn_3Be_7$ MG with a critical diameter of 2 mm (Kim et al., 2002). In 2005, Guo et al. (2005), by tuning the Cu/Ni ratio, developed $Ti_{40}Zr_{25}Be_{20}Ni_3Cu_{12}$ MG, with an enhanced glass forming critical diameter of 14 mm. This was because the high Cu content changed the competing phase in glass formation from quasi-crystalline to crystalline, indicating the key role of Cu in the GFA of TiZrBe series MGs. Then, Hao et al. (2006); Hao et al. (2009) examined the effect of Y on the GFA of $Ti_{40}Zr_{25}Be_{20}Ni_3Cu_{12}$ and found that with 0.5 at% Y addition, an MG rod of 5 mm in diameter could be fabricated with low-purity raw materials as Y scavenged oxygen and impurities, leading to the formation of the Laves phase. The effect of Nb on the GFA of $Ti_{40}Zr_{25}Be_{18}Cu_9Ni_8$ MG was investigated separately in Shan et al. (2008); Li et al., 2014), and no prominent enhancement was observed. Mei *et al.* examined the effect of Ta on the GFA of $Ti_{40}Ni_8Cu_9Be_{18}Zr_{25}$ MG but found deterioration in GFA (Mei et al., 2007). For applications such as lightweight high-strength materials, Duan et al. (2008) reported the fabrication of lightweight $Ti_{45}Zr_{20}Be_{35}$ (4.59 g/cm^3) and $Ti_{40}Zr_{25}Be_{30}Cr_5$ (4.76 g/cm^3) MGs containing no late transition metals with critical diameters of 6 and 8 mm. Following the path of TiZrBe series MGs, the best glass formers in Ti-based MG, $Ti_{32.8}Zr_{30.2}Be_{22.7}Ni_{5.3}Cu_9$ MG by Tang et al. (2010) and $Ti_{32.8}Zr_{30.2}Cu_9Fe_{5.3}Be_{22.7}$ MG by Zhang et al. (2015), were reported with a diameter over 50 mm comparable to the GFA of Zr-based (Lou et al., 2011) and Pd-based MGs (Nishiyama et al., 2012). **Figure 3** shows the 50-mm rod of $Ti_{32.8}Zr_{30.2}Cu_9Fe_{5.3}Be_{22.7}$ MG. The superior GFA was considered to be resulting from obedience to Inoue's rules and the confusion effect induced by the 5 constituent elements (Greer, 1993).

Gong et al., 2012a; Gong et al., 2012b; Gong et al., 2012c; Gong et al., 2013a; Gong et al., 2013b; Gong et al., 2013c; Gong et al., 2018; Gong et al., 2020) developed the TiZrBe (Fe, Al, Fe + Cu, Al + Cu, Co.) MGs, Zhao et al. (2014); Zhao et al. (2015a); Zhao et al. (2015b); Zhao et al. (2016) fabricated TiZrBe (Cu, Ni, Ag) MGs, and Gu et al. (2017); Gu et al. (2019a); Gu et al. (2019b) developed the TiZrBeNi and TiZrBeNi (Fe, Cu) MGs with high GFA of a critical diameter of centimeters. The high GFA of these MGs are generally ascribed to obedience to Inoue's rules and the large electronegativity of the composing elements. These MG systems largely enrich the family of TiZrBe series MGs. Lin *et al.* found that by adjusting the Ti/Zr ratio, the critical glass forming diameter of $Ti_{32.8}Zr_{30.2}Be_{22.7}Ni_{5.3}Cu_9$ MG could be enhanced to 20 mm (Lin et al., 2018). Similar results were also observed in $Ti_{35}Zr_{30}Be_{27.5}Cu_7$ MG (Song et al., 2019). This was attributed to the fact that the addition of Zr increases the content of icosahedral quasi-crystalline clusters, which stabilize the undercooled melt.

With the inclusion of light metal Be of small atomic size (0.111 nm in diameter), TiZrBe series MGs usually possess excellent GFA and are readily developed for lightweight structural materials with high strength. More efficiently, with the addition of Cu and another late transition metal like Fe and Ni, that is, coexistence of Cu + Ni, Cu + Fe, the critical diameter of TiZrBe-series MG would be improved to several centimeters. As stated before, the competing phases in glass formation, the mixing heat, the confusion effect, electronegativity, the atomic size ratio, the short range order of melt, etc. have been adopted to rationalize the high GFA of TiZrBe series MGs. However, the fundamental physics underpinning the superior GFA of TiZrBe-based MGs remains less clear. On the other hand, for the biotoxicity of Be and Ni, despite the excellent GFA in TiZrBe series MGs, the application of these MGs encountered great difficulty in the field of biomaterials. Thereby, to meet the demand of biomaterials, Ti-based MGs bearing no Ni and no Be were developed.

TiZrCu Series

TiZrCu series MGs as brazing filler metals were reported early in 1991 (Rabinkin et al., 1991). In 1994, by introducing Zr into the TiCuNi ternary system, Amiya et al., 1994) found that the TiZrCu ternary system and the TiZrCuNi quaternary system showed much improved thermal stability. For example, the amorphous $Ti_{50}Cu_{40}Zr_{10}$ powders prepared by high-pressure gas atomization showed a clear supercooled liquid region of 47 K. This is due to the large atomic size of Zr and the negative mixing heat of Zr–Cu, which increased the difficulty in the redistribution of constituent elements for crystallization. By introducing Zr and Ni into the TiCu binary system, for the atomic size mismatch and strong interaction induced, Men et al. (2005) reported the formation of

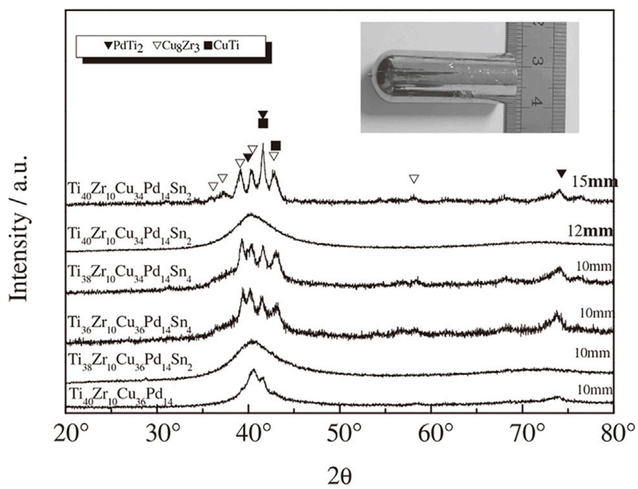

FIGURE 4 | XRD patterns of TiZrCuPdSn MGs. The inset is the 12 mm rod of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ MG (from Zhu et al. (2012a)).

$Ti_{45}Zr_5Cu_{45}Ni_5$ MG, with a critical diameter of 3 mm. However, $Ti_{45}Zr_5Cu_{45}Ni_5$ MG is still not Ni-free. As Pd and Ni belong to the same family, Zhu *et al.* proposed to replace Ni (0.125 nm) with Pd (0.137 nm) in the Ti–Cu–Ni–Zr system and prepared a Ni-free $Ti_{40}Zr_{10}Cu_{34}Pd_{16}$ MG, with a glass forming critical diameter of 6 mm (Zhu et al., 2007a; Zhu et al., 2007b). The improved GFA is due to the atomic size difference and the negative mixing heat between Pd and Ti, and Zr and Cu. By replacing Cu with Sn in $Ti_{40}Zr_{10}Pd_{14}Cu_{36}$ MG, as shown in **Figure 4**, Zhu *et al.* reported $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ and $Ti_{40}Zr_{10}Cu_{32}Pd_{14}Sn_4$ MGs with maximized GFA of a critical diameter of 12 mm in conjunction with high plasticity and strength (Zhu et al., 2008; Zhu et al., 2012a). This was also due to the atomic size difference and the negative mixing heat induced by Sn, proving the positive effect of Sn on Ti-based MGs. For the atomic size and mixing heat, Xie et al. (2010a) examined the effect of large atom Sn (0.141 nm) and small atom Ni (0.125 nm) on the GFA of $Ti_{45}Cu_{37.8}Zr_{10}Ni_{7.2}$ MG and found $(Ti_{0.45}Cu_{0.378}Zr_{0.10}Ni_{0.072})_{98}Sn_2$ MG and $Ti_{43.15}Zr_{9.59}Cu_{36.24}Ni_{9.06}Sn_{1.96}$ MG (Xie et al., 2010b) with increased GFA of a critical diameter of 2–3 mm.

Lately, Wang et al. (2013a) investigated the effect of Co. on the GFA of $Ti_{40}Zr_{10}Pd_{14}Cu_{36}$ MG and reported the $Ti_{39}Zr_{10}Pd_{14}Cu_{36}Co_1$ MG and the $(Ti_{0.39}Zr_{0.10}Pd_{0.14}Cu_{0.36})_{99}Co_1$ MG with critical diameters of 10 and 8 mm respectively. The increased GFA for the Co containing MG was attributed to the formation of network composed of Co,, Zr, and Pd atoms where the Co atoms connect with Zr and Pd atoms, as illustrated in **Figure 5**.

In 2010, Zhao *et al.* investigated the effect of Si addition on the GFA of $Ti_{43.89}Cu_{43.60}Zr_{6.75}Ni_{5.76}$ MG with a deep eutectic character (Zhao et al., 2010) and found that small addition (0.5–1 at%) would improve GFA for the negative mixing heat, the confusion effect, and possibly the scavenging effect of Si on O, and the destabilizing effect of Si on the TiO_2 cluster. By replacing Cu with Si, Zhu *et al.* found the formation of $Ti_{40}Cu_{33}Zr_{10}Pd_{14}Sn_2Si_1$ MG with increased thermal stability of an SLR of 80 K but reduced GFA (Zhu et al., 2012b). This was possibly due to the increase in the liquidus temperature induced by Si addition. Yi *et al.* also reported the preparation of $Ti_{45.0}Cu_{40.1}Zr_{12.7}Si_{2.2}$ MG, with a critical diameter of 3 mm (Yi, 2012). However, Tsai *et al.* studied the small addition effect of Si on the GFA of $Ti_{40}Zr_{10}Pd_{14}Cu_{36}$ MG (Tsai et al., 2015) and reported only slight variation in GFA. It is inferred that the effect of Si on TiZrCu series MGs is more prone to the enhancement of thermal stability.

In 2008, Qin *et al.* found that micro-addition of Nb in $Ti_{40}Zr_{10}Pd_{14}Cu_{36}$ MG would lead to the formation of *in situ* Pd_3Ti nanoparticle MG composites (Qin et al., 2008). Oak *et al.* examined the effect of Nb and Ta addition on the GFA of $Ti_{45}Zr_{10}Pd_{10}Cu_{31}Sn_4$ MG (Oak et al., 2009; Oak et al., 2011) and also found decreased GFA. Qin *et al.* found that the addition of Ta reduced the GFA of $Ti_{40}Zr_{10}Pd_{14}Cu_{36}$ MG but increased the corrosion resistance and plasticity (Qin et al., 2012). Fornell *et al.* investigated the effect of Nb on another $Ti_{40}Zr_{10}Cu_{38}Pd_{12}$ MG and found the formation of $CuTi_2$ and CuTi nanoparticles (Fornell et al., 2013). Qin *et al.* (Qin et al., 2016) further explored the effects of Au, Pt, Nb, and Ta replacing Cu on the GFA of $Ti_{40}Zr_{10}Pd_{14}Cu_{34}Sn_2$ MG and found decayed GFA with the precipitation of Pd_3Ti nanoparticles. The authors attributed this fact to the decreased crystallization temperature after micro-addition of these elements. Yang *et al.* investigated the effect of Nb addition on the GFA of $Ti_{40}Zr_{10}Cu_{33}Pd_{14}Sn_3$ and found the precipitation of β-Ti and Ti_2Cu phases (Yang et al., 2017a). Wu et al. (2019) also observed decreased GFA in $Ti_{40}Zr_{10}Cu_{33}Pd_{14}Sn_3$ MG with the addition of Nb. It is seen that the addition of Nb is detrimental to the GFA, and the resulting glass formation competing phases are complicated. The effect of Nb on GFA might be due to the positive mixing heat of Nb–Ti, Nb–Zr, and Nb–Cu.

Different attempts for new Ti-based MGs were also made, but the reason for the reduced GFA was not clear. In 2017, Oak *et al.* reported the preparation of $Ti_{45}Hf_{10}Pd_{10}Cu_{30}Sn_5$ MG by replacing Zr with Hf in $Ti_{45}Zr_{10}Pd_{10}Cu_{30}Sn_5$ MG, however with reduced GFA (Oak et al., 2017). Jia et al. (2018) studied the effect of Ni and Pt replacing Pd on the GFA of Ti41Cu36Zr10Pd13 and also found the degradation of GFA. By replacing Cu with Ag, Nicoara *et al.* designed and prepared $Ti_{30}Zr_{32}Ag_7Pd_{24}Sn_7$ MG ribbons (Nicoara et al., 2018) with marginal GFA. Tantavisut *et al.* reported the fabrication of Ti44Zr10Pd10Cu6Co23Ta7, Ti44Zr10Pd10Cu10Co19Ta7, and Ti44Zr10Pd10Cu14Co15Ta7 MGs (Tantavisut et al., 2018). Bera *et al.* characterized the effect of Ga replacing Cu on the GFA of $Ti_{40}Zr_{10}Pd_{14}Cu_{36}$ MG and reported GFA in $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Ga_2$ and $Ti_{40}Zr_{10}Cu_{32}Pd_{14}Ga_4$ MGs, with a diameter of 3 mm (Bera et al., 2019). They found that they could only obtain $Ti_{40}Zr_{10}Pd_{14}Cu_{36}$ MG of 2 mm diameter and attributed the GFA in $Ti_{40}Zr_{10}Cu_{32}Pd_{14}Ga_4$ MG to the larger atomic size and more negative mixing heat of Ga.

To remove Ni from $Ti_{47.4}Cu_{42}Zr_{5.3}Ni_{5.3}$ MG, Seki *et al.* prepared $Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3}$ (TM = Co., Fe) MGs but with decreased thermal stability (Seki et al., 2008) due to the difference in the electronic state between Ni and Co or Fe. Yin *et al.*

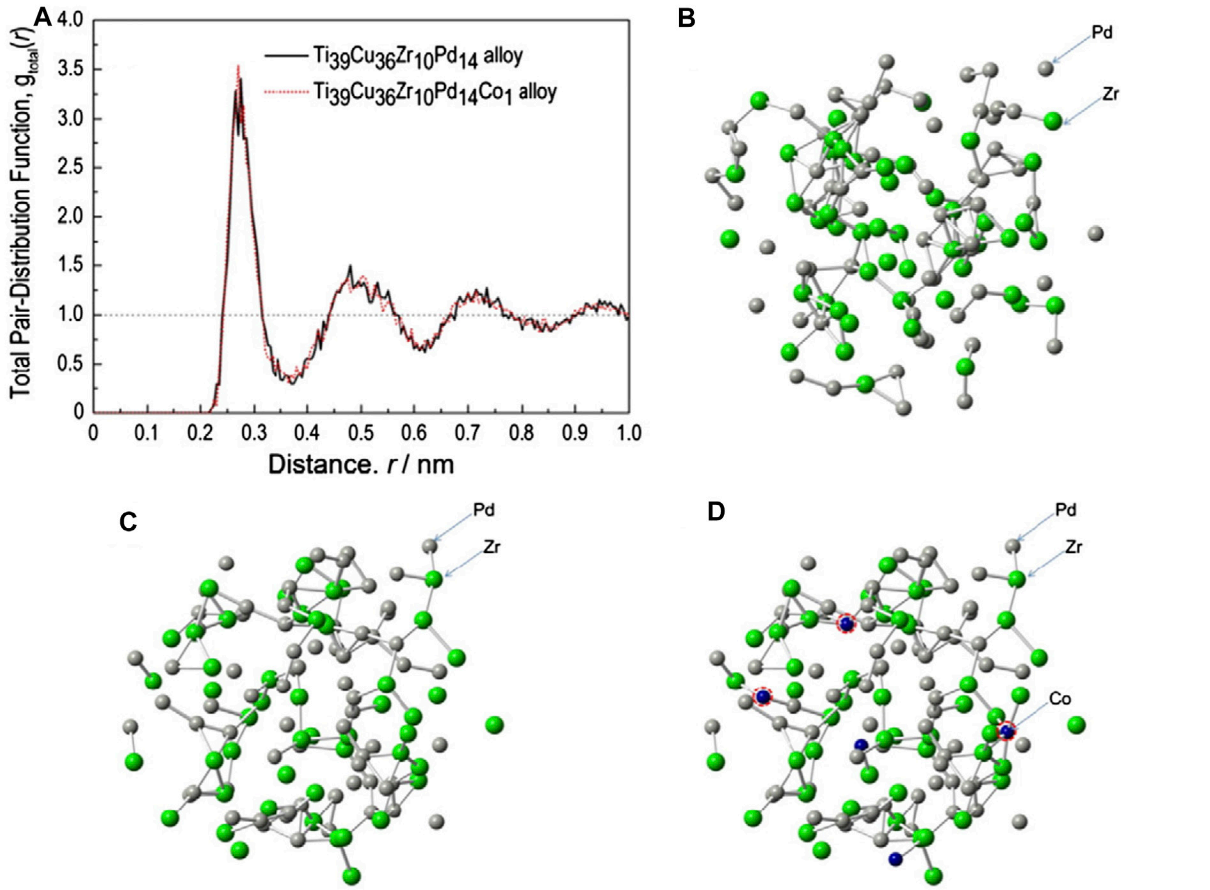

FIGURE 5 | Atomic structures in $Ti_{39}Zr_{10}Cu_{36}Pd_{14}$ and $Ti_{39}Zr_{10}Cu_{36}Pd_{14}Co_1$ MGs obtained from MD simulations (from Wang et al. (2013a)). **(A)** Total pair-distribution function; **(B)** arrangements of Pd and Zr in $Ti_{39}Zr_{10}Cu_{36}Pd_{14}$; **(C)** arrangements of Pd and Zr in $Ti_{39}Zr_{10}Cu_{36}Pd_{14}Co_1$; **(D)** arrangements of Pd, Zr, and Co in $Ti_{39}Zr_{10}Cu_{36}Pd_{14}Co_1$ MG.

examined the effect of Ni replacing Cu on $Ti_{45.8}Zr_{6.2}Cu_{45}Sn_2Si_1$ MG and that of Zr replacing Ti on $Ti_{52}Cu_{40.9}Ni_{5.1}Sn_2$ MG and prepared MGs, with a critical diameter of 4 mm (Yin et al., 2013). They proposed that the GFA of these MGs showing multiple crystallization events correlated strongly with the onset temperature of the last crystallization event. Using the cluster-plus-glue-atom model, Wang *et al.* designed 2 TiZrCuSn MGs (i.e., $(Ti_{7.2}Zr_{1.8})$ $(Cu_{8.72}Sn_{0.28})$ and $(Ti_{7.2}Zr_{1.8})$ $(Cu_{8.45}Sn_{0.55})$), with a critical glass forming diameter of 5 mm (Wang et al., 2013b), and later $Ti_{40}Zr_{10}Cu_{56.94}Sn_{3.06}$ and $Ti_{45.71}Zr_{11.43}Cu_{39.29}Sn_{3.57}$ MGs (Wang et al., 2016). However, for the high atomic fraction of Cu, they are more like Cu-based MGs, except for $Ti_{45.71}Zr_{11.43}Cu_{39.29}Sn_{3.57}$ MG. Based on Inoue's rules and the effective atomic radius, Shirasawa *et al.* prepared TiZrCo ternary MGs around a predicted near eutectic $Ti_{44}Zr_{30}Co_{26}$ MG (Shirasawa et al., 2014), as shown in **Figure 6**. These results provide possible routes for the design of new Ti-based MGs. Cao *et al.* studied the effect of nitrogen on the GFA of $Ti_{42.5}Cu_{40}Zr_{10}Ni_5Sn_{2.5}$ and reported that the addition of N of 0.1 at% could facilitate the formation of glass by suppressing the formation of the competing eutectic structure (Cao et al., 2016). Kuball *et al.* reported the fabrication of a new class of sulfur-bearing Ti-based Ti75Ni17S8 and $Ti_{40}Zr_{35}Cu_{17}S_8$ MGs (Kuball et al., 2018; Kuball et al., 2019). The effect of S on GFA was interpreted with its smaller size, higher mixing heat with other elements, low solubility in intermetallics, and the tendency for formation of covalent bonds. Introducing small metalloid atoms could be new paths for the development of Ti-based MGs.

In 2014, Hu *et al.* reported $Ti_{47}Zr_{7.5}Cu_{40}Co_{2.5}Sn_2Si_1$ and $Ti_{45}Zr_{7.5}Cu_{42}Co_{2.5}Sn_2Si_1$ MGs, with a critical diameter of 3 mm (Hu et al., 2014). Coincidently, Wang *et al.* also studied the effect of Zr and Si on the GFA of $Ti_{46}Cu_{44}Co_7Sn_3$ MG and reported the $Ti_{46}Zr_{11.5}Cu_{31.5}Co_7Sn_3Si_1$ MG, with a critical diameter of 3 mm (Wang et al., 2015a). The improved GFA was due to the atomic size difference and mixing heat induced by Zr and Si. Later, they examined the effect of Ag replacing Cu on the GFA of $Ti_{46}Cu_{31.5}Zr_{11.5}Co_7Sn_3Si_1$ MG and found that $Ti_{46}Cu_{27.5}Zr_{11.5}Co_7Sn_3Si_1Ag_4$ MG showed a critical diameter of 4 mm (Wang et al., 2015b). This was inspired by the fact that Pang et al. (2015) reported the preparation of $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ MG with a diameter of 7 mm, as shown in **Figure 7**, the largest Ni-, Be-, and Pd-free Ti-based MG as the addition of silver promoted the formation of icosahedral clusters in the undercooled melt, which suppressed the nucleation

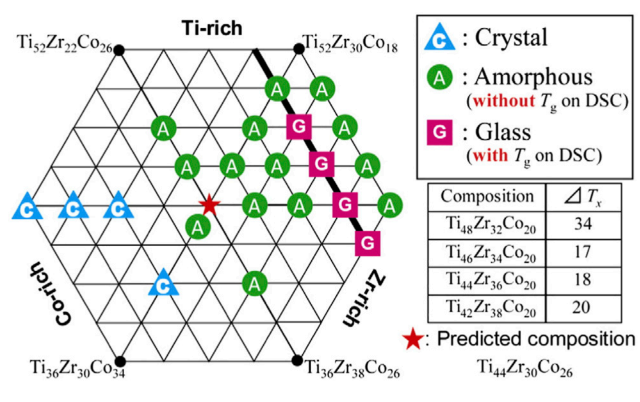

FIGURE 6 | Design of TiZrCo ternary MGs (from Shirasawa et al. (2014)).

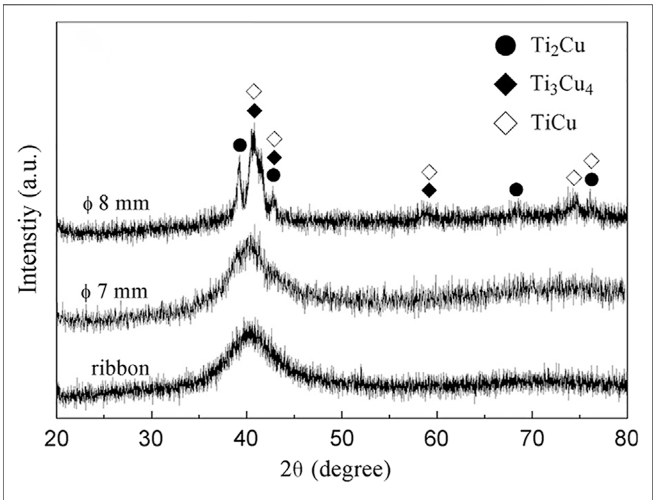

FIGURE 7 | XRD patterns of $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ MG (from Pang et al. (2015)).

of competing crystalline phases. Yan *et al.* investigated the effect of Nb replacing Cu on the GFA of $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ MG, but observed reduced GFA of a critical diameter of 3 mm (Yan et al., 2018). This result was ascribed to the positive mixing heat of Nb–Ti, Nb–Zr, and Nb–Cu. The effect of (Ti + Zr)/Cu ratio on the glass formation in $(TiZrCu)_{95}Fe_{2.5}Sn_2Si_1$ MG was also studied and was found that $Ti_{47}Zr_{7.5}Cu_{40}Fe_{2.5}Sn_2Si_1$ MG exhibited good GFA, with a critical diameter of 3 mm (Liu et al., 2016a). Later, they examined the effect of Sc replacing Ti on the GFA of $Ti_{47}Cu_{40}Zr_{7.5}Fe_{2.5}Sn_2Si_1$ MG and reported best glass formers $Ti_{45}Cu_{40}Zr_{7.5}Fe_{2.5}Sn_2Si_1Sc_2$ and $Ti_{44}Cu_{40}Zr_{7.5}Fe_{2.5}Sn_2Si_1Sc_3$ MGs with a critical diameter of 6 mm (Liu et al., 2016b), for the scavenging effect of Sc and its negative mixing heat with Si, Sn, Zr, and Cu. They also found that Ta replacing Cu reduced the GFA of $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ MG (Liu et al., 2020a) for the positive mixing heat of Ta-(Ti, Zr, Cu). Yang *et al.* from the same group also examined the GFA in $(Ti, Cu, Zr)_{92.5}Fe_{2.5}Sn_2Si_1Ag_2$ alloys with composition adjustment between Ti, Cu, and Zr (Yang et al., 2021). Wang *et al.* examined the effect of Pd replacing Cu on the GFA of $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ MG (Wang et al., 2021) and found reduced GFA for the increased liquidus temperature with Pd addition. However, the critical diameter was still no more than 7 mm.

The search for Be-, Ni-, and Pd-free TiZrCu series MG with high GFA has been a hot topic up to now. In the past decades, great efforts have been made to reduce the content of Pd in $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ MG and increase the GFA. For this purpose, vastly different elements have been alloyed with TiZrCu series MGs, for example, Pd, Sn, Si, Ni, Nb, Hf, Ta, Fe, Ag, Co, N, S, and Sc. Also, coexistences of Pd + Sn and Pd + Co. would benefit glass formation. However, just like the situation in TiZrBe and TiCuNi series MGs, the fundamental physics underlying glass formation in Ti-based MGs remains elusive as vastly different concepts have been adopted to rationalize the intractable variation of GFA with the addition of alloying elements. Particularly, for the septenary and octonary alloys, understanding the GFA becomes increasingly difficult. On the other hand, the large atomic fraction of copper which would lead to adverse tissue reactions (Long and Rack, 1998) and also poses a disadvantage for the application of TiZrCu series MGs as biomaterials.

TiZrSi Series

MGs composed merely of non-toxic elements are highly desirable for biomedical applications. The TiZrSi system (Whang et al., 1985), an important system in Ti-based crystalline alloys, was focused on to this motive. However, compared to other 3 series of Ti-based MGs, the TiZrSi series MGs are highly vulnerable in glass formation. Polk et al. (1978) examined the glass formation behaviors in TiSi and TiNi binary and TiNiSi ternary systems and reported a typical $Ti_{60}Ni_{30}Si_{10}$ MG processable by melt spinning but with considerable Ni content. They proposed that low liquidus temperature, chemical difference, and size difference were critical to glass formation. In 1980, Suryanarayana *et al.* reported the formation of binary TiSi MG containing 15–20 at% Si (Suryanarayana et al., 1980). Inoue *et al.* reported the preparation of TiNb(Ta)Si(Mo, Rh, Ru, Ir, B, C, Ge) MG for the research on superconducting in MGs (Inoue et al., 1980a; Inoue et al., 1980b; Inoue et al., 1981). In 1992, Tarasova investigated the short range order of $Ti_{64}Zr_{22}Si_{14}$ MG (Tarasova et al., 1992). Oak *et al.* prepared thin ribbon $(TixZryTaz)_{85}Si_{15}$ MGs and found that the $Ti_{60}Zr_{10}Ta_{15}Si_{15}$ MG ribbon of 20 μm in thickness exhibited both high ductility and ultimate strength (Oak and Inoue, 2007). In 2008, Oak *et al.* not only examined the glass formation in TiZrPdSi system but also prepared amorphous ribbons of 20 μm thickness (Oak and Inoue, 2008), despite the fact that the TiZrPdSi system obeyed Inoue's 3 rules. The authors argued that the TiZrPdSi system would be a possible seed system for the development of Ti-based MGs bearing no toxic elements. Bai *et al.* prepared the biocompatible $Ti_{70}Zr_6Fe_7Si_{17}$ MG and $Ti_{64}Zr_5Fe_6Si_{17}Mo_6Nb_2$ MG and predicted that the addition of Mo and Nb should increase the GFA for the obedience to Inoue's rules, but the specimen remained in the ribbon shape with a thickness of 80 μm (Bai et al., 2008). As shown in **Figure 8**, Calin

TABLE 1 | Best glass formers of several metallic glasses.

Composition	Critical diameter (mm)	Method	Year	Ref
$Hf_{43}Zr_4Cu_{31.25}Ni_{9.75}Al_{12}$	18	Water quenching	2021	Saini et al. (2021)
$Hf_{40}Zr_9Cu_{31}Ni_8Al_{12}$				
$Ni_{60}Pd_{20}P_{14}Si_2B_4$	25	Fluxing + water quenching	2020	Zeng et al. (2020)
$Cu_{46}Zr_{33.5}Hf_{13.5}Al_7$	28.5	Water quenching	2020	Saini et al. (2020)
$Gd_{55}Co_{17.5}Al_{27.5}$	8	Copper mold casting	2019	Shao et al. (2019)
$Al_{86}Ni_{6.75}Co_{2.25}Y_{3.25}La_{1.75}$	2.5	Fluxing + copper mold casting	2017	Yang et al. (2017b)
$Ce_{70}Ga_8Cu_{22}$	20	Copper mold casting	2015	Zhou et al. (2015)
$Cr_{45}Fe_{11}Co_7Mo_{14}C_{15}B_6Y_2$	8	Copper mold casting	2015	Xu et al. (2015)
$Cr_{30}Fe_{26}Co_7Mo_{14}C_{15}B_6Y_2$				
$(Fe_{0.8}Co_{0.2})_{47}Cr_{15}Mo_{14}C_{15}B_6Tm_3$	18	Copper mold casting	2013	Suryanarayana and Inoue (2013)
$Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$	80	Fluxing + water quenching	2012	Nishiyama et al. (2012)
$Ag_{38.5}Mg_{30.8}Ca_{23.1}Cu_{7.7}$	4	Inverted injection casting	2012	Laws et al. (2012)
$Zr_{46}Cu_{30.14}Ag_{8.36}Al_8Be_{7.5}$	73	Copper mold casting	2011	Lou et al. (2011)
$Co43Fe_5Cr_{15}Mo_{14}C_{15}B_6Er_2$	15	Copper mold casting	2011	Zhang et al. (2011)
$Au_{40}Si_{17.20}Cu_{28.30}Ag_{5.7}Pd_5$	6	Copper mold casting	2009	Guo et al. (2009)
$Mg_{59.5}Cu_{22.9}Ag_{6.6}Gd_{11}$	27	Copper mold casting	2007	Zheng et al. (2007)
$La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}Ni_5Co_5$	30	Water quenching	2007	Jiang et al. (2007)
$Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$	20	Fluxing + water quenching	2004	Schroers and Johnson (2004)
$Ca_{65}Mg_{15}Zn_{20}$	15	Copper mold casting	2004	Park and Kim (2004)
$Y_{36}Sc_{20}Al_{24}Co_{20}$	25	Water quenching	2003	Guo et al. (2003)

The numbers in the compositions are subscripts.

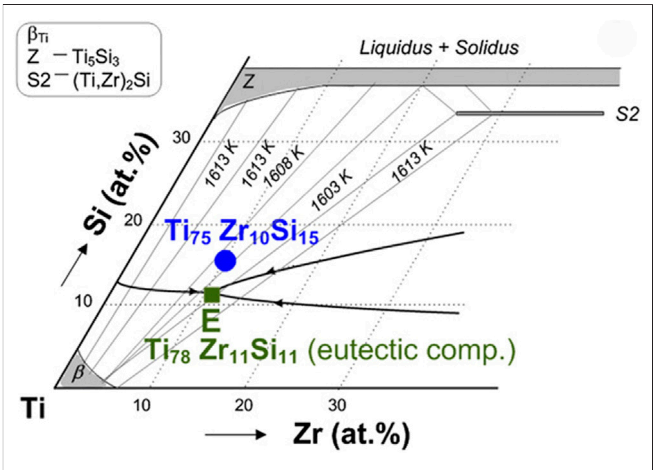

FIGURE 8 | Composition design of TiZrSi MG (from Calin et al. (2013)).

et al. developed $Ti_{75}Zr_{10}Si_{15}$ and $Ti_{60}Nb_{15}Zr_{10}Si_{15}$ MG ribbons of 30 μm in thickness with better biocompatibility and found that the addition of Nb increases the GFA for atomic mismatch and negative mixing heat of Nb-Si (Calin et al., 2013).

Other alloys, for example, $Ti_{64}Zr_{10}Si_{15}Nb_{11}$ and $Ti_{56}Zr_{10}Si_{15}Nb_{19}$, were also prepared in ribbons but containing nanoparticles (Gabor et al., 2019). Huang *et al.* reported the fabrication of thin ribbon $Ti_{42}Zr_{40}Si_{15}Ta_3$ and $Ti_{40}Zr_{40}Si_{15}Cu_5$ MGs of 80–100 μm thickness (Huang et al., 2014; Huang et al., 2016) and found that for using as biomaterials, the content of Cu should be less than 5 at%, although it benefited GFA. Wu *et al.* investigated the effect of Sn on the GFA of $Ti_{60}Zr_{10}Ta_{15}Si_{15}$ MG (Wu et al., 2014) and found that the addition of Sn reduced the GFA. The authors attributed this fact to the relative decrease in the Si content with the addition of Sn, which reduces the atom pairs (Ti-Si) of negative mixing heat and is of great atomic size mismatch. Guo *et al.* fabricated the TiFeSi, TiFeSi(Zr,Pd,Ge) MGs (Guo et al., 2015) near the eutectic composition $Ti_{65}Fe_{30}Si_5$ and found that small additions of Zr will ease glass formation, but the presence of Ge and Pd promotes crystallization for the atomic size mismatch. Abdi *et al.* studied the $Ti_{75}Zr_{10}Si_{15}$ and $Ti_{60}Zr_{10}Nb_{15}Si_{15}$ alloys and found that by melt spinning only glassy matrix composites of 30–50 μm in thickness could be obtained (Abdi et al., 2016). These results suggest that the GFA of $Ti_{75}Zr_{10}Si_{15}$ and $Ti_{60}Zr_{10}Nb_{15}Si_{15}$ MGs is not robust. Although poor GFA, the $Ti_{60}Nb_{15}Zr_{10}Si_{15}$ MG thin film was found to exhibit excellent biocompatibility (Thanka Rajan et al., 2019). Based on a design approach for high entropy alloys, Calin et al. (2021) prepared $Ti_{20}Zr_{20}Nb_{20}Hf_{20}Si_{20}$, $Ti_{30}Zr_{25}Nb_{25}Si_{15}Ga_3B_2$, and $Ti_{20}Zr_{20}Nb_{20}Hf_{20}Si_{15}Ga_3B_2$ alloys to obtain better glass former; however, slight crystalline phases precipitated in the glassy matrix.

Compared to the other 3 series of MGs, the GFA of TiZrSi series MGs is quite poor, as evidenced by the fact that only ribbon samples could be fabricated in the discovered compositions. This is largely because aiming for biomaterials, the development of TiZrSi series MGs excludes the presence of most late transition metals which are either adverse to the human body or noble. According to the empirical rules for glass formation, the late transition metals of medium atomic sizes compared to large early transition metal atoms and small metalloid atoms are critical in the GFA of MGs. As evidence suggests, the best glass formers in other MG systems are given in **Table 1**. It is seen that these alloy systems generally consist of early transition metals (ETMs), late transition metals (LTM), metal elements, and metalloids. More importantly, late transition metals (Cu, Ni, Co., Zn, Ag, Pd, etc.) are a prerequisite for their excellent GFA either as the base element or as the main constituents. As also observed in Zhao et al. (2015b), compared to electronegativity and mixing enthalpy, larger atomic size difference generally leads to higher GFA and seems more dominant for Ti-based MGs, whereas the mixing enthalpy and the electronegativity are also important. Thereby, to make a breakthrough and develop new TiZrSi series MGs, more advanced and instructive understandings on the GFA of Ti-based MGs is of top priority. On the other hand, as a compromise for the development of biomaterials, addition of expensive elements Pd, Hf, Ta, etc. would be tolerable on a condition that enough GFA could be achieved. Nevertheless, there is still a long journey before the fabrication of toxic element free Ti-based MGs.

CONCLUDING REMARKS

In retrospect, on the development paths of Ti-based MGs, it is seen that the basic method for the design of MG forming compositions mainly includes the following 3 steps: i) according to the 3 empirical rules of Inoue, usually 3 main composing elements are chosen by their atomic sizes and the mixing heat between them; ii) the eutectic compositions are usually taken as guides for the base composition; and iii) the addition of minor alloying elements chosen by Inoue's rules or substituting the main elements with similar elements by the confusion principle was performed to optimize the GFA of the base composition with trial and error." However, the factors that play a non-trivial role on GFA are far more than those covered by the 3 empirical rules of Inoue—the eutectic composition, and the confusion principle. This fact significantly reduces the efficiency of the basic method. In this sense, in order to develop novel Ti-based MGs, as presented before, of top priority is to advance current understandings on the GFA of MGs—for instance, the coexistence of elements on GFA. More recently, the novel strong correlation between GFA and the full width at half maximum of the first diffraction peak of MGs (Li et al., 2021a) would help rapidly identify best glass formers.

On the other hand, based on the advances in artificial intelligence and manufacture technology, there could be 2 other ways around the aforementioned difficulty to fabricate bulk size Ti-based MGs. First is the machine learning approach (Sun et al., 2017). As outlined in *Development paths of Ti-based MGs*, large quantity of data on the glass formation behaviors of Ti-based MGs have been accumulated in the past half century. For the large number of Ti-based MG compositions observed and the many different alloying elements adopted, it is pretty difficult to manually establish a self-consistent GFA model compatible with all the data. In recent years, machine learning models for materials design boom up because of its ability in analyzing large-volume and high-dimension data and have proved to be a promising approach for finding MG compositions with good GFA (Sun et al., 2017; Liu et al., 2020b; Xiong et al., 2021). With machine learning models, based on the glass forming compositions and the non-glass forming compositions accumulated to date, potential Ti-based MGs with high GFA could be more conveniently found.

Second is the 3D printing technique (Zhang et al., 2021). It has been long noticed that the thermal stability and the GFA of MGs are usually decoupled. As the fundamental physics in glass formation is the suppression of crystal formation, a possible reason for the decoupling between GFA and thermal stability could arise from the discrepancy between the crystal nucleation activation energy and the crystal growth activation energy. We argue that those MGs with high thermal stability tend to have high crystal nucleation activation energy, which enables large undercooling of liquid, while those MGs with high GFA, besides high crystal nucleation activation energy, tend to have high crystal growth activation energy which suppresses the burst growth of crystal nuclei. This is partially validated by recent work on 3D printing of MGs (Ouyang et al., 2021). For the rapid cooling process in the 3D printing process, the thermal stability of MGs weighs much over the GFA. Thereby, by the 3D printing technique, with MG powders of excellent thermal stability, the size limit on the fabrication of Ti-based MGs would be ultimately relieved. A similar approach is the ultrasonic assisted forming (Ma et al., 2019), by which giant MGs are successfully prepared (Li et al., 2021b). This processing method also provides a potential way for the fabrication of bulk size Ti-based MGs containing no noble, no toxic, and no heavy metal elements as long as Ti-based MGs have high enough thermal stability to survive the processing period.

AUTHOR CONTRIBUTIONS

All authors have made substantial, direct, and intellectual contribution to the work and approved it for publication.

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