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Tantalum based bulk metallic glasses

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ABSTRACT

Ta-based bulk metallic glasses with high strength (2.7 GPa) and hardness (9.7 GPa), high elastic modulus (170 GPa) and high density (12.98 g/mm^3) were developed. The best glass forming ability so far for a Ta–Ni–Co system reaches a critical diameter of 2 mm by the copper mold casting method. It shows an exceptionally high glass transition temperature of 983 K and a high crystallization temperature up to 1023 K. The unique mechanical and physical properties make them a promising high strength material.

I. Introduction

The development of a novel bulk metallic glasses (BMGs) system has drawn great attention due to their unique physical, chemical and mechanical properties [1–3]. A large number of multi-component BMG systems with excellent glass forming ability (GFA), e.g. Pd- and Zr-based BMGs with critical diameters larger than 1 cm [1–4] and some binary BMG systems such as CuZr [5], Ni–Nb [6] and NiTa [7], have been developed. Some BMG systems have been found to show interesting phenomena, such as super large plasticity at room temperature in Zr-based amorphous alloy [8], very high fracture strength (more than 5000 MPa) in Co-based metallic glasses [9], excellent corrosion resistance in Ni-based amorphous alloys [10], rare earth based BMGs with functional physical properties [3,11], and very low glass transition temperature close to room temperature in Ce- and Sr-based glassy alloys [12,13]. Obviously, there are commercial and scientific interests to find new excellent glass-forming systems accompanying unique mechanical and physical properties.

Tantalum (Ta) is an element with high density (16.654 g/cm^3), high elastic moduli (its Young's modulus is 186 GPa and bulk modulus is 200 GPa) and high melting point (3290 K). According to the elastic moduli criterion [3], the Ta based metallic glasses could have unique mechanical and physical properties. In fact, Ta is usually used as a minor addition element in the enhancement of GFA and properties of various BMGs. For example, it is found that Ta can be added in Zr-based BMGs to precipitate crystal particles which lead to the superior mechanical performances [14]. The Ta-based amorphous alloys have been reported to be formed by different ways, such as Ta–Cu [15] amorphous films by magnetron sputtering, Au–Ta [16], Ta–Zr [17] and Ta–Rh [18] amorphous films by ion mixing, Ta–Ni [19], Ta–Fe [20] and $Ta_{55}Zr_{10}Al_{10}Ni_{10}Cu_{15}$ [21] amorphous powders by mechanical alloying. Recently, a Ni-rich binary BMG system such as $Ni_{60}Ta_{40}$ BMG had been developed [7]. However, the Ta-based BMGs quenching from the liquid alloy have not been reported so far.

In this work, we report the development of Ta-based bulk metallic glasses in a ternary Ta–Ni–Co system by a conventional copper mold suction casting technique. The obtained Ta-based BMGs show high density, high glass transition temperature (T_g) and onset temperature of crystallization (T_x), high fracture strength and micro-hardness (Hv), and high Young's modulus (E) compared with most BMG-forming systems such as Zr-, Pd-, Ni-, Cu-, Fe-, Mg- and rare earth-based BMGs. The finding of the novel Ta-based BMGs enriches the member of the BMG family and has application potentials.

2. Experimental

TaNiCo master alloys were prepared by arc melting of pure Ta, Ni and Co (>99.5%) under a purified argon atmosphere. These alloys were re-melted at least 4 times to ensure the chemical homogeneity. Then, the alloy rods with different diameters were prepared by copper mold suction casting. And the amorphous ribbons were prepared by the melt-spinning technique. The structure and phase of as-cast rods and ribbons were examined by X-ray diffraction (XRD) using a MAC M03 diffractometer with Cu *Ka* radiation. Thermal properties and characteristic temperatures were examined by high temperature differential scanning calorimetry (DSC) in NETZSCH DSC 404F3 Pegasus under a purified argon atmosphere with a heating rate of 10 K min^{-1}. The T_g, T_x, melting point T_m, and liquidus temperature T_l of the metallic glasses were determined with an accuracy of ± 2 K. Vickers hardness of the bulk glassy samples was obtained by a micro-hardness tester with an accuracy of ± 0.05 GPa. The uniaxial compression tests were performed by an Instron 5500R1186 machine

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at a strain rate of 5×10^{-4} s^{-1} and the length–diameter ratio of the specimens is 2:1. The accuracy of the yielding stress is about ±0.005 GPa. The density ρ was measured by Archimedes' principle in alcohol with an accuracy of 0.5%. At least three specimens were used per samples for each of the technique.

3. Results

A Ni-rich binary BMG system such as $Ni_{60}Ta_{40}$, $Ni_{62}Ta_{38}$ BMGs had been developed [7]. Fig. 1(a) shows the XRD patterns of as-cast rods of Ta–Ni–Co ternary alloys with a diameter of 2 mm. The optimized $Ta_{42}Ni_{40}Co_{18}$ composition shows only a board scattering peak without distinct incisive diffraction peaks of crystalline phases. The XRD patterns of $Ta_{42}Ni_{42}Co_{16}$ and $Ta_{42}Ni_{38}Co_{20}$ rods with composition adjacent to $Ta_{42}Ni_{40}Co_{18}$ also have a board scattering peak, but there are some diffraction peaks of crystalline phases such as CoTa, Ni_3Ta and Ni_2Ta intermetallic compounds superpose in the board diffused glassy peak. The results indicate that the GFA of the Ta-based BMG is very sensitive to the minor composition change and the composition range to form the 2-mm-diameter Ta–Ni–Co BMG rods is narrow. We find that the $Ta_{42}Ni_{40}Co_{18}$ alloy has the best glass forming ability among the ternary TaNiCo alloys. The DSC curve of the $Ta_{42}Ni_{40}Co_{18}$ rod in Fig. 1(b) shows an obvious glass transition at 983 K and a sharp crystallization peak at 1023 K, which further confirms the glassy state of the alloy. The high values of T_g and T_x indicate the high thermal stability of the metallic glass, which is in favor of industrial application [1–3].

To study the glass-forming ability, the DSC measurements were performed for a series of $Ta_{42}Ni_{42-x}Co_{16+x}$ ($x=0$, 2, 4, and 6) glassy ribbons and the DSC traces are shown in Fig. 2. The T_g, T_x, melting point T_m, liquidus temperature T_l, reduced glass transition temperature T_{rg} ($=T_g/T_l$), supercooled liquid region ΔT_x ($=T_x-T_g$) and γ [$=T_x/(T_g+T_l)$] of these alloys are listed in Table 1. From the DSC traces, one can see that both T_g and T_x have slight changes as the Ni content decreases from 42 to 36 at.% and Co content increases from 16 to 22 at.%. When the value of x increases, T_g increases to 1005 K and T_x decreases slightly. The composition of $Ta_{42}Ni_{42}Co_{16}$ has a lower melting point among these alloys. $Ta_{42}Ni_{40}Co_{18}$,

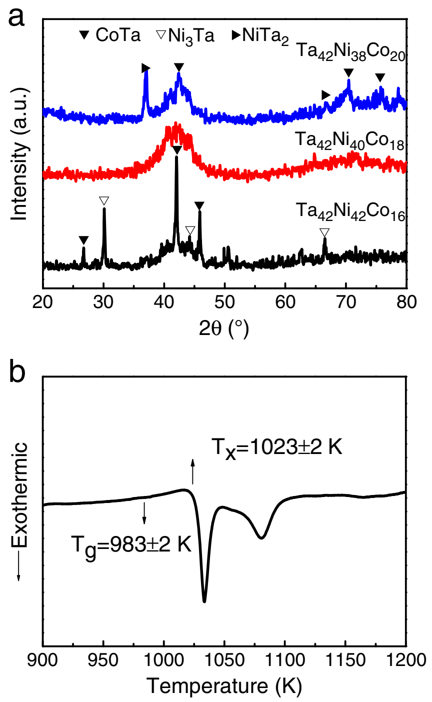

Fig. 1. (a) The XRD curves of as-cast Ta-based glassy rods with a diameter of 2 mm. (b) DSC trace of the $Ta_{42}Ni_{40}Co_{18}$ glassy rod at a heating rate of 10 K/min.

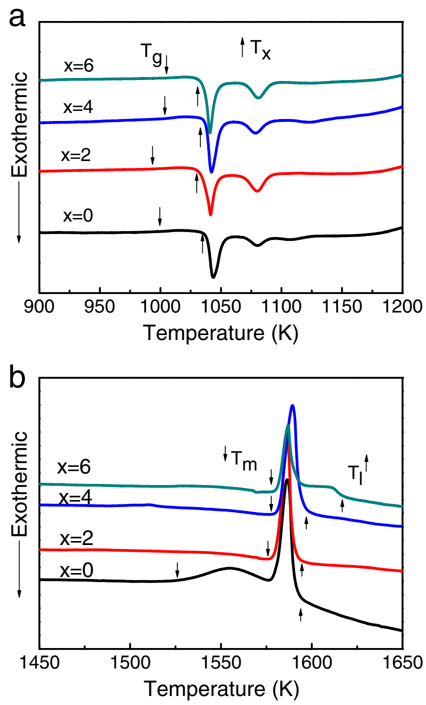

Fig. 2. The DSC curves of $Ta_{42}Ni_{42-x}Co_{16+x}$ glassy ribbons with a heating rate of 10 K/min. (a) Glass transition and crystallization. (b) Melting.

$Ta_{42}Ni_{38}Co_{20}$ and $Ta_{42}Ni_{36}Co_{22}$ have a similar melting behavior with an increasing T_l. This result indicates that the TaNiCo alloy deviates from the eutectic point when Co content increases. With the x increasing, ΔT_x and γ gradually decrease from 40 K to 30 K and from 0.401 to 0.395, respectively. While T_{rg} does not vary in a regular way like other alloy systems and is in the range of 0.621–0.628. Based on Turnbull's theory [22], the amorphous alloy could be fabricated easily when $T_{rg}\approx2/3$ and the GFA increases as T_{rg} increases. The γ values for a system with good GFA normally are in a range of 0.350–0.500 [23]. Compared with the Zr-based BMGs with similar T_{rg} or γ whose critical diameters are about 10 mm [24], the GFA of the Ta–Ni–Co system is relative low. The best glass forming alloy of $Ta_{42}Ni_{40}Co_{18}$, which has critical diameters about 2 mm, does not have the largest ΔT_x, T_{rg} or γ among the TaNiCo alloys. These parameters for predicting GFA do not reflect the change of GFA of these alloys well. The changes of the thermal properties of the Ta–Ni–Co system with the variation of Ta and Ni contents are also listed in Table 1. The minor addition can significantly and effectively tune the GFA of a BMG forming system [24]. It is expected that the suitable minor addition could significantly improve the GFA of the ternary TaNiCo alloy, which is our further work.

The fracture strength σ and the elastic modulus of 2-mm glassy rods of $Ta_{42}Ni_{40}Co_{18}$ BMG are obtained from compressive tests. This BMG shows a high fracture strength (σ) of 2740 MPa and a high E of ~170 GPa, which are similar with that of previously reported in Ni-based BMGs [25]. The elastic constants of BMGs, which are dependent

Table 1
The thermal properties of Ta-based glasses.

Alloys	T_g ($\pm$2 K) (K)	T_x ($\pm$2 K) (K)	T_m ($\pm$2 K) (K)	T_l ($\pm$2 K) (K)	ΔT_x ($\pm$2 K) (K)	T_{rg}	γ
$Ta_{42}Ni_{42}Co_{16}$	998	1038	1527	1592	40	0.627	0.401
$Ta_{42}Ni_{40}Co_{18}$	993	1032	1578	1593	39	0.623	0.399
$Ta_{42}Ni_{38}Co_{20}$	1003	1038	1580	1596	35	0.628	0.399
$Ta_{42}Ni_{36}Co_{22}$	1005	1035	1581	1617	30	0.621	0.395
$Ta_{46}Ni_{36}Co_{18}$	991	1027	–	–	35	–	–
$Ta_{50}Ni_{32}Co_{18}$	980	1015	–	–	35	–	–

on that of their constituents, correlate with the mechanical properties [26]. The Poisson's ratios of Ta, Ni and Co are 0.34, 0.31, and 0.31, respectively [15], and the Poisson's ratio of this alloy is then relatively small according to the elastic moduli criterion [26]. It is known that the intrinsic plasticity or brittleness of BMGs correlates with Poisson's ratio ν [8]. The larger the ν is, the more ductile the BMGs become. Therefore, it is reasonable that the $Ta_{42}Ni_{40}Co_{18}$ BMG with low Poisson's ratios shows brittle behavior.

We compare the fracture strength σ, micro-hardness Hv, density, and T_g of the Ta-based BMG with that of other different glass forming systems as shown in Fig. 3 (Data are from Refs. 1–4, 7, and 23,). We note that these parameters especially the fracture strength measured by a compression test were determined using the same procedure by different groups. It can be seen from Fig.3(a) that the $Ta_{42}Ni_{40}Co_{18}$ BMG has higher fracture strength and high glass transition temperature similar to Ni-based BMGs. Fig. 3(b) shows the relation between E and T_g in different BMG-forming systems. The high Young's modulus of this BMG due to the high modulus of the Ta element roughly

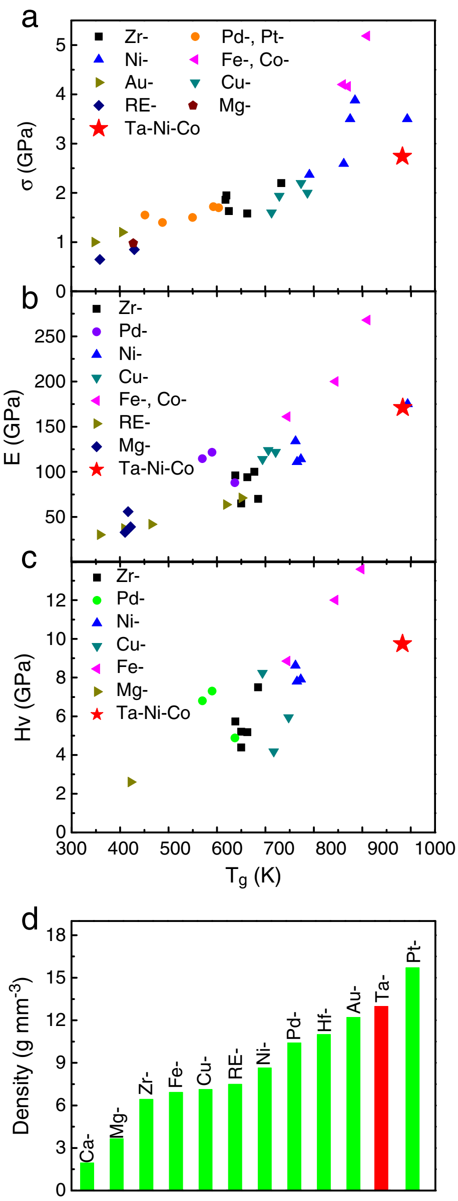

Fig. 3. Comparisons of (a) strength and T_g, (b) E and T_g, and (c) Hv and T_g in different BMG-forming systems. (d) Comparison of density of BMGs and that of their main constituents. Data come from Ref. 22 and 24–27.

correlates to its high T_g [26]. The micro-hardness of $Ta_{42}Ni_{40}Co_{18}$ BMG is 9.74 GPa, which is much higher than that of most BMGs [see Fig. 3 (c)]. The density of $Ta_{42}Ni_{40}Co_{18}$ BMG is 12.98 g mm^{-3}, which is close to that of Pt-based BMGs [27], but much higher than that of Pd-, Fe-, Hf-, Zr- and RE-based BMGs [28–30] [See Fig.3(d)].

4. Discussion

The unique properties of the Ta-based BMGs can be attributed to that of the Ta element which has the higher elastic moduli, strength and density among the metal elements. According to elastic moduli correlations, the elastic constants M of BMGs show a correlation with a weighted average of the elastic constants M_i for the constituent elements as [26]: $M^{-1} = \sum f_i \cdot M_i^{-1}$, where f_i denotes the atomic percentage of the constituent. Sufficient data on elastic moduli and properties of BMGs exhibits that there are clear correlations [26]. For example, the higher value of elastic modulus gives higher T_g which is also verified in this work (see Fig.3). The established correlations between elastic moduli and properties are our guidelines for the development of the BMGs by appropriate composition selection of components. The Ta element content can effectively modulate the properties of the Ta-based BMGs, and the properties of Ta-based BMGs, such as elastic moduli and density, are controlled by Ta content. The result further confirms the route for designing new metallic glasses with good properties by selection of components with suitable elastic moduli.

5. Conclusions

A ternary Ta-based BMG system was developed by a copper mold casting technique. The optimized $Ta_{42}Ni_{40}Co_{18}$ BMG has the best glass forming ability, which can be cast into 2-mm glassy rods. The BMG exhibits very high thermal stability, high glass transition temperature and high crystallization temperature. The glass also has excellent mechanical properties such as high micro-hardness, high Young's modulus and high fracture strength, and high density. The combined properties of the Ta-based BMGs may be a probable candidate of the effective kinetic energy penetrators.

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References

[1] A. Inoue, Acta Mater. 48 (2000) 279.
[2] A.L. Greer, E. Ma, MRS Bull. 32 (2007) 611.
[3] (a) W.H. Wang, Adv. Mater. 21 (2009) 4524;
(b) Q. Luo, W.H. Wang, J. Non-Cryst. Solids 355 (2009) 759.
[4] A. Inoue, N. Nishiyama, H. Kimura, Mater. Trans., JIM 38 (1997) 179.
[5] M.B. Tang, D.Q. Zhao, M.X. Pan, W.H. Wang, Chin. Phys. Lett. 21 (2004) 901.
[6] L. Xia, W.H. Li, B.C. Wei, Y.D. Dong, J. Appl. Phys. 99 (2006) 026103.
[7] Y.M. Wang, Q. Wang, J.J. Zhao, C. Dong, Scr. Mater. 63 (2010) 178.
[8] Y.H. Liu, G. Wang, R.J. Wang, D.Q. Zhao, M.X. Pan, W.H. Wang, Science 315 (2007) 1385.
[9] A. Inoue, B. Shen, H. Koshiba, H. Kato, A.R. Yavari, Nat. Mater. 2 (2003) 661.
[10] A. Kawashima, H. Habazaki, K. Hashimoto, Mater. Sci. Eng., A 304–306 (2001) 753.
[11] S. Li, R.J. Wang, M.X. Pan, D.Q. Zhao, W.H. Wang, J. Non-Cryst. Solids 354 (2008) 1080.
[12] (a) B. Zhang, D.Q. Zhao, M.X. Pan, W.H. Wang, A.L. Greer, Phys. Rev. Lett. 94 (2005) 205502;
(b) B. Zhang, D.Q. Zhao, M.X. Pan, R.J. Wang, W.H. Wang, Acta Mater. 54 (2006) 3025.
[13] (a) K. Zhao, J.F. Li, D.Q. Zhao, W.H. Wang, Scr. Mater. 61 (2009) 1091;
(b) W. Jiao, K. Zhao, X.K. Xi, D.Q. Zhao, M.X. Pan, W.H. Wang, J. Non-Cryst. Solids 356 (2010) 1867.
[14] J.S.C. Jang, S.R. Jian, D.J. Pan, Y.H. Wu, J.C. Huang, T.G. Nieh, Intermetallics 18 (2010) 560.

[15] F. Zeng, Y. Gao, L. Li, D.M. Li, F. Pan, J. Alloys Comp. 389 (2005) 75.
[16] F. Pan, Y.G. Chen, Z.J. Zhang, B.X. Liu, J. Non-Cryst. Solids 194 (1996) 305.
[17] O. Jin, B.X. Liu, J. Non-Cryst. Solids 211 (1997) 180.
[18] W.C. Wang, J.H. Li, Y. Dai, B.X. Liu, Scr. Mater. 59 (2008) 3.
[19] C.H. Lee, T. Fukunaga, J. Mater. Sci. Lett. 21 (2002) 141.
[20] C.K. Lin, P.Y. Lee, J.L. Yang, C.Y. Tung, N.F. Cheng, Y.K. Hwu, J. Non-Cryst. Solids 232–234 (1998) 520.
[21] M.S. El-Eskandarany, W. Zhang, A. Inoue, J. Alloys Comp. 350 (2003) 222.
[22] D. Turbull, Contemp. Phys. 10 (1969) 473.
[23] S. Guo, Z.P. Lu, C.T. Liu, Intermetallics 18 (2010) 883.
[24] W.H. Wang, Prog. Mater. Sci. 52 (2007) 540.
[25] M.W. Chen, Annu. Rev. Mater. Res. 38 (2008) 445.
[26] W.H. Wang, J. Appl. Phys. 99 (2006) 093506.
[27] J. Schroers, W.L. Johnson, Phys. Rev. Lett. 93 (2004) 255506.
[28] C. Suryanarayana, A. Inoue, Bulk Metallic glasses, CRC Press, Boca Raton, 2011.
[29] (a) J.F. Li, D.Q. Zhao, M.L. Zhang, W.H. Wang, Appl. Phys. Lett. 93 (2008) 171907;
(b) W.H. Wang, C. Dong, C.H. Shek, Mater Sci. Eng., R 44 (2004) 45;
(c) Z.F. Zhao, Z. Zhang, P. Wen, M.X. Pan, D.Q. Zhao, Z. Zhang, W.H. Wang, Appl. Phys. Lett. 82 (2003) 4699.
[30] L. Zhang, L.L. Shi, J. Xu, J. Non-Cryst. Solids 355 (2009) 1005.