LETTER TO THE EDITOR

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Letter to the Editor

Distinguish bonding characteristic in metallic glasses by correlations

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ABSTRACT

By statistically analyzing 48 kinds of metallic glasses, we report clear correlations between the dimensionless ratio of glass transition temperature/Debye temperature (T_g/Θ_D) and density (ρ), and between Young's modulus or shear modulus and T_g/ρ, for the glasses consisting of only metal elements, while the metallic glasses alloyed with metalloid elements exhibit distinct deviation from the correlations. It is suggested that the alloying of metalloid elements would show covalent-like bonding characteristics in metallic glass, and the found correlations can be used to distinguish different bonding characteristics in metallic glasses.

The bonding nature and the atomic structure are of vital importance in determining the properties of condensed matter [1]. For metallic glasses, it is also believed that the local atomic structure and bonding nature determine various properties, such as glass-forming ability, glass transition, fracture strength, and plasticity [2–5]. Intensive work has been dedicated in characterizing the local atomic packing structures and the atomic bonding natures of metallic glasses. The bonding nature of metallic glass, which depends mainly on the atomic packing structures, would vary for different systems especially for the systems that contain metalloid elements. Various metalloid elements have been added to metallic glasses for improving their glass-forming ability [6–9] and mechanical or physical properties [6,10–13]. In crystalline compounds, the metalloid elements usually combine other elements with covalent or ionic bonding. The alloying of metalloid elements in metallic glasses would also change the metallic characteristic such as the electrical conduction behavior and electronic specific heat contribution [10,14,15]. However, it is still unclear about the different roles of the metalloid and metal elements in glass formation and properties.

Studying the correlations between the various properties of metallic glasses can help us to understand the commonness among different systems and to contrast different roles of specific element or parameter in glass formation and properties. Hitherto, lots of correlations among the thermodynamic, kinetic, elastic and physical properties of metallic glasses have been found [3,16–23]. Particularly, the elastic moduli correlations help us in searching new systems with specific properties [17–19]; the correlation between the Poisson's ratio and the fragility of glass-forming liquid [17,18,20] is important for understanding the inheritance character between liquids and glasses; the correlation between the cluster symmetry and glass-forming ability [3] exhibits the microstructural origin for glass-forming ability; the glass transition temperature and strength correlation provides the insight into the fracture mechanism of metallic glasses [21], and so on. With the development of more metallic glasses with unique properties, more and more experimental data have been collected. This would permit more new correlations to be found which is of vital importance in understanding the nature of metallic glasses.

In this letter, we studied the correlation between the elastic constants (including Young's modulus E and shear modulus G), Debye temperature Θ_D, glass transition temperature (T_g), and density (ρ) by analyzing 48 different kinds of metallic glasses (listed in Table 1). It is found that clear correlations exist between Θ_D (or E, or G) and T_g/ρ in the 37 metallic glasses consisting of only metallic elements. The other 10 metallic glasses alloyed with metalloid elements, however, deviate markedly from the correlations. We suggest that the alloying of metalloid elements would show covalent bonding characteristics in metallic glasses, and the correlations can be used to distinguish the bonding characteristics in metallic glasses.

The Θ_D and elastic moduli shows correlation with T_g in metallic glasses as shown in Fig. 1(a). In the physics point of view, both the two characteristic temperatures, T_g and Θ_D, reflect the nature of the atomic bonding [17,18,21]. However, it can be seen that the correlation between T_g and Θ_D is rough. The scattering of this correlation might derive from the different atomic bindings. When T_g is scaled with ρ, obviously, the values of T_g/ρ show much better correlation with Θ_D for the 37 kinds of metallic glasses consisting of only metallic elements [see Fig. 1(b)] The alloying of metalloid elements results in bigger density and Θ_D in the metallic glasses and obvious deviation from the correlation as shown in Fig. 1(b), denoting that the alloying of metalloid elements makes the metallic glasses stronger in atomic bonding. The G and E of the 37 kinds of metallic glasses consisting of metallic elements also show clear linear relationship with T_g/ρ as shown in Fig. 2(a) and (b). And the metalloid-alloyed metallic glasses also markedly deviate from the correlations and their elastic moduli tend to be bigger. This indicates that the characteristic energy of glass

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Table 1
The compositions, T_g/ρ, molar mass M, Debye temperature Θ_D, E, G, K, and ρ of various 48 kinds of metallic glasses . (data are from Refs. [17–19,22])

Composition	T_g/ρ (K cm^3/g)	M (g/mol)	Θ_D (K)	E (GPa)	G (GPa)	K (GPa)	ρ (g/cm^3)
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	90.56	79.01	282.0	101.1	36.9	128.2	8.304
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	100.62	59.94	320.0	97.8	36.1	113.0	6.162
$Ti_{40}Zr_{25}Ni_3Cu_{12}Be_{20}$	120.84	53.15	338.0	96.2	35.5	109.6	5.445
$Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$	102.07	65.47	306.0	96.0	35.3	113.7	6.447
$(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{84}Al_{16}$	106.49	70.09	294.0	95.1	35.2	106.7	6.545
$Zr_{40}Ti_{15}Cu_{11}Ni_{11}Be_{21.5}Mg_{0.5}Y_1$	103.40	60.06	315.0	94.2	34.7	109.8	6.044
$Zr_{48}Nb_8Cu_{14}Ni_{12}Be_{18}$	97.68	68.78	295.0	93.9	34.3	118.8	9.190
$(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{85.7}Al_{14.3}$	104.64	70.97	291.0	92.4	33.9	112.3	6.585
$(Cu_{50}Zr_{50})_{94}Al_6$	94.96	74.36	282.4	92.4	33.8	113.8	7.129
$(Zr_{55}Al_{15}Cu_{20}Ni_{10})_{98}Y_2$	107.02	73.12	286.0	92.0	33.8	110.5	6.559
$Zr_{41}Ti_{14}Cu_{12.5}Ni_2Be_{22.5}Fe_8$	104.51	59.72	314.0	91.6	34.0	99.6	5.932
$(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{88}Al_{12}$	101.58	72.15	288.0	91.1	33.4	111.5	6.704
$(Cu_{50}Zr_{50})_{90}Al_7Gd_3$	90.56	76.25	277.1	90.1	33.2	105.8	7.122
$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$	100.94	76.52	274.0	87.0	31.9	106.7	6.806
$(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{90}Al_{10}$	97.48	73.17	279.0	85.9	31.3	112.1	6.740
$(Zr_{55}Al_{15}Cu_{20}Ni_{10})_{96}Y_4$	106.25	73.44	278.0	85.9	31.5	104.8	6.438
$Zr_{65}Al_{10}Ni_{10}Cu_{15}$	98.16	77.39	266.9	83.0	30.3	106.7	6.642
$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}B_1Al_{10}$	99.50	76.63	266.0	82.4	30.0	108.2	6.764
$Tm_{55}Al_{25}Co_{20}$	81.94	111.45	216.0	72.2	25.6	62.0	8.274
$Er_{50}Y_6Al_{24}Co_{20}$	83.62	107.23	218.0	71.0	27.0	65.1	7.785
$Er_{55}Al_{25}Co_{20}$	81.28	110.53	215.0	70.7	27.1	60.7	8.157
$Ho_{55}Al_{25}Co_{20}$	82.28	109.24	210.0	66.6	25.4	58.8	7.888
$Dy_{46}Y_{10}Al_{24}Co_{20}Fe_2$	88.99	103.02	214.0	64.2	24.4	58.5	7.046
$Tb_{36}Y_{20}Al_{24}Co_{20}$	95.44	93.26	222.0	63.6	24.0	60.5	6.583
$Gd_{40}Y_{16}Al_{24}Co_{20}$	90.84	95.39	218.0	62.2	23.5	58.0	6.486
$Dy_{55}Al_{25}Co_{20}$	83.99	107.91	205.0	61.4	23.5	52.2	7.560
$Tb_{55}Al_{25}Co_{20}$	81.73	105.94	203.0	59.5	22.9	50.2	7.488
$(Mg_{65}Cu_{25}Gd_{10})_{99}Ti_1$	107.87	47.00	275.7	52.3	19.9	47.8	3.940
$Mg_{60}Cu_{25}Gd_{15}$	98.82	54.06	261.0	52.2	19.9	46.6	4.220
$Nd_{60}Al_{10}Fe_{20}Co_{10}$	69.11	106.30	190.8	51.7	19.8	44.3	7.018
$Pr_{55}Al_{25}Co_{20}$	79.87	96.03	190.0	45.9	17.4	43.5	6.373
$La_{55}Al_{25}Cu_{10}Ni_5Co_5$	79.85	95.38	183.0	41.9	15.6	44.2	5.836
$Pr_{60}Al_{10}Ni_{10}Cu_{20}$	59.49	105.82	160.0	37.2	13.6	45.2	6.875
$Pr_{60}Cu_{20}Ni_{10}Al_{10}$	59.28	105.82	160.0	37.2	13.6	45.2	6.900
$Ce_{68}Al_{10}Cu_{20}Co_2$	52.13	111.87	146.1	31.3	11.8	30.3	6.752
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	53.82	113.01	144.0	30.3	11.5	27.0	6.670
$Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$	58.32	125.39	131.0	26.5	10.4	19.8	6.516
Metalloid elements alloyed BMGs							
$Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$	100.96	59.48	335.0	105.6	39.5	107.8	6.171
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	63.29	73.70	279.4	99.8	35.5	172.6	9.259
$Pd_{40}Ni_{40}P_{20}$	61.93	72.24	292.0	108.3	38.6	185.1	9.413
$Pd_{64}Fe_{16}P_{20}$	62.77	83.24	256.0	93.0	33.1	161.8	10.037
$Ni_{80}P_{20}$	75.98	53.15	324.0	102.8	36.9	159.0	8.133
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	61.29	72.94	280.0	98.1	35.1	158.5	9.137
$Pd_{77.5}Si_{16.5}Cu_6$	58.46	90.92	250.0	98.1	34.8	181.6	10.777
$(Fe_{60}Cr_{10}Mo_9C_{13}B_6Er_2)_{95}Cu_5$	103.65	53.43	451.4	191.3	72.8	171.4	7.921
$Fe_{60}Cr_{10}Mo_9C_{13}B_6Er_2$	104.85	52.90	471.0	205.5	79.2	169.1	7.916
$Pd_{32}Ni_{48}P_{20}$	63.98	68.42	295.0	104.9	37.5	173.4	6.715
$Fe_{48}Cr_{15}Mo_{14}C_{15}B_6Er2$	108.42	53.83	483.0	218.9	83.6	191.0	7.849

transition, which is represented by k_BT_g, depends not only on the bonding strength but also on the mass density of the glass.

The alloying of metalloid elements results in obvious deviation from the found correlations, this is because it would induce some covalent-like bonds between the metalloid and metallic elements which strengthens and shortens the atomic bonding. The metalloid and metallic elements usually have large negative mixing heat which favors the formation of strong atomic bonding [11]. Some of the small metalloid elements can also act as interstitial atom to cause the dense structure [11].

The density of an alloy has close relation with its bonding characteristics such as bonding length and angle. Thus, the density of the metallic glasses should differ from the weighted average density of the component elements due to the atomic bonding in the glass, and the density change reflects the bonding characteristics. Fig. 3 shows the difference between the measuring density ρ_{ex}, and the weighted average value ρ_{av}, in the form of $(\rho_{ex}-\rho_{av})/\rho_{av}$ versus V_{mol} ($V_{mol}=M/\rho_{ex}$, M is the average molar mass). The ρ_{av} is calculated according to Ref. [17] as: $\rho_{av}^{-1} = \sum_i f_i\rho_i^{-1}$ (ρ_i is the density of the ith crystalline compositional element; f_i is the atomic concentration of the ith composition element). The data of density of metallic glasses is from Refs. [17] and [22]. The density variation of the BMGs with only metal components is less than 8%. While the metalloid-alloyed systems show larger density variation deriving from the large negative mixing heat between metalloid and metallic atoms [4]. The alloying of white phosphorus ($\rho=1.823$ g/cm^3) induces the largest density variation of about 17%–27% [If use violet phosphorus ($\rho=2.340$ g/cm^3), the change decreases to around 7%–15%]. This is because the strength of the covalent bonds in the P alloyed metallic glasses is much stronger than the van der Waals' force in the white P crystal. Carbon, boron and silicon have strong bonds with the metallic elements, and the length of the bonds would decrease when they are alloyed with metal elements, which is certified by the increased of density, as shown in Fig. 3. Even 1 at.% alloying of carbon in Zr-based

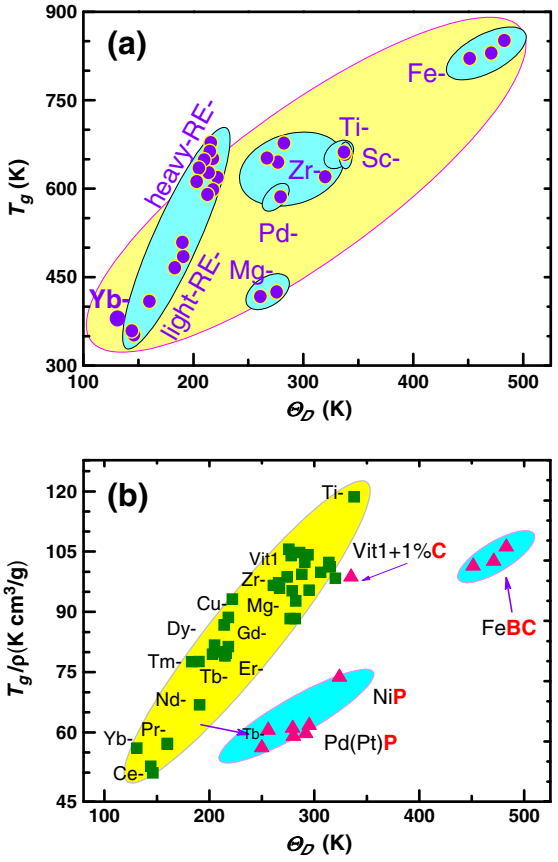

Fig. 1. (a) The T_g show rough correlation with Debye temperature (Θ_D). (b) The T_g when scaled with density shows clear correlation with Θ for the 37 metallic glasses consisting of only metal elements. The 10 metalloid-alloyed metallic glasses markedly deviate from the correlation.

BMG increases the density because the small carbon atoms perform as interstitial atoms and would tighten the amorphous structure [11]. Thus, the alloying of metalloid elements would tighten the amorphous structure by strengthening and shortening the atomic bonds,

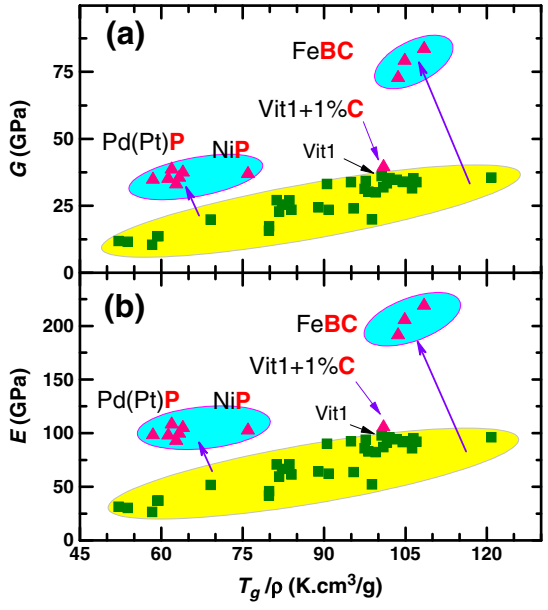

Fig. 2. The elastic moduli, (a) G and (b) E, show good correlation with T_g/ρ for the metallic glasses consisting of only metal elements, and metalloid-alloyed metallic glasses markedly deviate from the correlation.

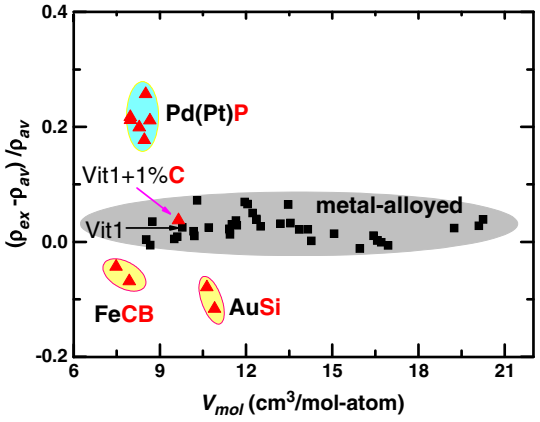

Fig. 3. The relative changes of density after amorphization versus molar volume.

and increase the local packing density. This result helps understanding the metalloid-induced large deviation phenomena in Figs. 2 and 3. On the other hand, the difference (~10%) between the calculated and actual density can explain the discrepancy reported in different works that use the calculated density instead of the measured density [21].

In summary, based on the systematical statistics of many different kinds of metallic glasses, we find that the Debye temperature, E, and G show good correlation with the T_g scaled with density for those metallic glasses with only metallic components. The alloying of metalloid elements induces obvious deviation from the correlations. This suggests that the metalloid elements form covalent-like bonding in metallic glasses which tightens the atomic structure by strengthening and shortening the atomic bonds. The work also indicates that the correlations can be used to distinguish the metallic glasses with different bonding characteristics.

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