Correlation between fragility and cooperativity in bulk metallic glass-forming liquids

M. Ikeda*, M. Aniya

Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

*Corresponding author

Abstract

It is known that the structural relaxation in supercooled liquid and glassy metals exhibit a non-Debye type relaxation behavior and a VFT-like temperature dependence. Such behaviors are often characterized by the exponent of the Kohlrausch-Williams-Watts (KWW) function and by the value of the fragility. In the present work, a quantity N_B which gives the number of structural units involved in the thermally activated viscous flow is introduced to characterize the bulk metallic glass-forming liquids. N_B is defined from the Bond Strength – Coordination Number Fluctuation (BSCNF) model of the viscosity. It is shown that N_B can be a new indicator that quantifies the degree of cooperativity within the bulk metallic glass-forming liquids. For several bulk metallic glass-forming liquids, it is shown that the characteristic temperature ratio T_0/T_g, N_B, and the stretched exponent β_{KWW} are mutually correlated through the fragility index m derived from the BSCNF model.

Keywords: B. Glasses, metallic; B. Thermal properties; E. physical properties, miscellaneous

1. Introduction

Among the fields of material science, studies on bulk metallic glasses (BMGs) are one of the most actively debated fields of research, covering fundamental to applied aspects [1,2]. The BMGs, which are mostly multicomponent systems, have unique properties such as extraordinary high strength, low ductility, high hardness, excellent corrosion resistance, which permit the study of thermophysical properties in the supercooled liquid state [3-5]. To exploit their properties, better fundamental understandings of BMGs are necessary. The aim of the present work is to provide a theoretical framework to understand the relaxation behavior of BMGs.

In the analysis of the temperature dependence of the viscosity of amorphous metallic alloys, the Vogel-Fulcher-Tammann (VFT) equation has been quite often employed [6-11]. It is known that the VFT equation reproduces well the experimental data. However, the analysis based on a single use of the VFT equation is not sufficient to fully understand the physics behind the structural relaxation. For instance, the Vogel temperature or the ideal glass transition temperature T_0 which is one of the parameters in the VFT equation is not observed in real systems [12]. On the other hand, we have proposed that the Bond Strength – Coordination Number Fluctuation (BSCNF) model, which describes the temperature dependence of the viscosity of the melt, could provide an alternative description for the VFT equation.

The BSCNF model, which was originally introduced by one of the authors [13], describes the temperature dependence of the viscosity in terms of the mean values of the bond strength E_0, the coordination number Z_0, and their fluctuations, ΔE, ΔZ, of the structural units that form the melt. In our study, it has been found that when $|\Delta E|/E_0 = |\Delta Z|/Z_0$ is satisfied, the viscosity behavior described by the BSCNF model corresponds

exactly to that described by the VFT equation. That is, the BSCNF model incorporates the VFT description. This coincidence provides a way to understand the relaxation behavior from a microscopic point of view, regarding the bonding connectivity among the structural units. We do not need to rely on the ideal glass transition temperature T_0 in the analysis. This advantage comes from the fact that, the quantities used in the BSCNF model such as E_0, Z_0, ΔE, and ΔZ, are in principle measurable quantities. Therefore, it is expected that by using the BSCNF model, further insights on the viscous flow can be extracted which have not been revealed in the analysis by the VFT equation. On this regard, we have already shown that, a quantity N_B, which is defined from the BSCNF model [14], gives the number of structural units involved in the thermally activated viscous flow. It has been also shown that N_B can be expressed analytically with the BSCNF model parameters [15], and is closely related with the well-known concept of "cooperatively rearranging region (CRR)" in the theory of Adam and Gibbs [16]. Furthermore, from a theoretical side, we have obtained a relationship that connects the characteristic temperature ratio T_0/T_g to the parameters used in the BSCNF model. Here, T_g is the glass transition temperature.

In this work, the expressions for the cooperativity described by N_B and a relationship that describes the characteristic temperature ratio T_0/T_g are applied to analyze the relaxation behavior of bulk metallic glass-forming liquids. It is shown that the following three quantities, the ratio T_0/T_g, N_B, and the exponent of the Kohlrausch-Williams-Watts (KWW) function β_{KWW}, are mutually correlated through the fragility index m derived from the BSNCF model.

2. Fragility and cooperativity described by the BSCNF model

2.1 Fragility and characteristic temperature ratio T_0/T_g

It is widely accepted that the viscous behaviours of any kinds of glass-forming liquids are characterized by the fragility [17]. Mathematically, the fragility index m is defined by $m=\mathrm{d}\log\eta/\mathrm{d}(T_\mathrm{g}/T)|_{T=T\mathrm{g}}$ [18]. In general, the fragility of a bulk metallic glass-forming liquid exhibits an intermediate value between strong and fragile systems [2,3,6]. According to the BSCNF model, the fragility index m is expressed as [13,15]

$$m = \frac{1}{\ln(10)}\left\{\frac{B - C + 2\left[\ln\left(\frac{\eta_{T\mathrm{g}}}{\eta_0}\right) + \frac{1}{2}\ln(1 - B)\right]}{1 - B}\right\}, \qquad (1)$$

where $\eta_{T\mathrm{g}}$ and η_0 are the viscosity at T_g and at the high temperature limit, respectively. B and C appearing in Eq. (1) are the fitting parameters of the BSCNF model [13]. They are defined as

$$B = \frac{(\Delta E)^2(\Delta Z)^2}{R^2 T_\mathrm{g}^2}, \quad \text{and} \quad C = \frac{E_0 Z_0}{R T_\mathrm{g}}. \qquad (2)$$

Here, R is the gas constant. It has been reported that the fragility index m of a BMG is correlated with the elastic properties such as the shear and bulk modulus [2,19,20].

Meanwhile, the characteristic temperature ratio T_0/T_g can be equivalent to the fragility, because the ratio T_0/T_g takes the values between 0 (the strongest) and 1 (the most fragile) [21]. In the past, some analytical expressions for T_0/T_g have been proposed. For instance, in one of them, T_0/T_g is expressed in terms of the fragility index m and the

strength parameter D of the VFT equation [22]. On the other hand, using the parameters of the BSCNF model, the ratio T_0/T_g can be described as

$$\frac{T_0}{T_g} = 1 - \frac{\left(\frac{1+\sqrt{B^*}}{1-B^*}\right)C^* - \frac{1}{2}\ln(1-B^*)}{\ln(10)\,m} \quad . \tag{3}$$

Here, B^* and C^* denote the values of B and C that obey the following relation

$$C = \frac{2\gamma(1-B)}{2\gamma+\sqrt{B}(1+\gamma^2)}\left\{\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right\} \quad , \quad \text{where} \quad \gamma = \frac{|\Delta E|/E_0}{|\Delta Z|/Z_0} = 1. \tag{4}$$

Recently, we have found that for the case of γ=1, the viscosity behaviors described by the BSCNF model and by the VFT equation become identical. Here, it must be noted that B^* and C^* in Eq. (3) are calculated as a function of the fragility index m; $B^*(m)$ and $C^*(m)$. That is, the values of B^* and C^* are uniquely determined when the fragility index m is given. This observation is illustrated in Fig. 1. In this figure, the behavior of Eq. (4) with the values of $\eta_{Tg}=10^{12}$ Pa·s and $\eta_0=10^{-5}$ Pa·s is shown together with the behavior of the fragility index constant line. The intersection of the fragility index constant line (broken line) with the curve described by Eq. (4) (solid curve) gives the values of B^* and C^*. The point of the intersection is denoted as P in Fig. 1. Eq. (3) was also applied to investigate the viscosity of some polymers [23].

2.2. Cooperativity among the structural units that form the melt: N_B

An interesting quantity defined as $N_B=E_\eta/(E_0Z_0)$ has been proposed in the light of the BSCNF model [14]. Here, E_η is the activation energy for the viscous flow, and the product E_0Z_0 is the average total binding energy per one structural unit. Physically, N_B

gives the number of the structural units involved in the thermally activated viscous flow, and is expected to provide the degree of fluidity within the glass-forming liquids.

We have also found that N_B can be expressed analytically with B and C as [15],

$$N_B = \frac{B^* - C^* + 2\left\{\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B^*)\right\}}{(1-B^*)C^*} \quad . \tag{5}$$

Note that by connecting Eq. (5) to the fragility index m described in Eq. (1), N_B is expressed as $N_B=\ln(10)m(B^*,C^*)/C^*$. This relationship is an important result obtained in this study, since it provides the connection between the fragility and the cooperativity of the melt. The result suggests that the elastic properties, which are correlated with the fragility [19, 20], could be understood in terms of the cooperativity described by N_B.

In the next section, we will show the behaviors of T_0/T_g, N_B, and the exponent of the Kohlrausch-Williams-Watts (KWW) function β_{KWW} as a function of the fragility index m. Besides, we will discuss the correlation between the fragility and the cooperativity in bulk metallic glass-forming liquids in the light of the BSCNF model.

3. Results and discussion

Fig. 2 shows the relationship between the characteristic temperature ratio T_0/T_g and the fragility index m for eighteen bulk metallic glass-forming liquids. The materials considered and their parameters used in this study are indicated in Table 1. The three curves drawn in Fig. 2 are reproduced with Eq. (3) by varying the values of η_{Tg} and η_0. Zhao et al. have discussed the relation between the characteristic temperature ratio T_0/T_g and the fragility of glass-forming metallic systems [7]. In their analysis, the relation $T_0/T_g = 1 - m_1/m$ is used. Here, m_1 is a constant $m_1 = 16 \pm 2$ [7]. Basically, this relation is the same

to our relation, Eq. (3). However, there is a difference between the both relations. In Eq. (3), the term corresponding to m_1 is described with B^* and C^*. Thus, Eq. (3) contains more microscopic information which is not included in the relation, $T_0/T_g = 1 - m_1/m$. Intuitively, in our model, B gives the degree of the binding energy fluctuations and C gives the degree of total binding energy, respectively.

The relation between N_B and the fragility is shown in Fig. 3. From this figure, it is seen that N_B calculated from Eq. (5) follows the same trend to T_0/T_g shown in Fig. 2. The symbols are the same to those used in Fig.2. We have already mentioned that N_B is related with the cooperatively rearranging region (CRR). According to calorimetric experiments measuring the size of the cooperativity [24], it has been reported that CRR increases with the decrease in the temperature. It has been also shown that the more fragile the system is, the larger CRR are observed. CRR is thought as a region in which a subsystem can rearrange into another configuration without interacting thermally with neighbouring subsystems [25]. The entropy-based theory proposed by Adam and Gibbs, which is one of the most well-accepted models, explains the CRR of the glass-forming liquids in such a way that, the configurational entropy $S_c(T)$ decreases with the decrease in the temperature, resulting in the cooperative rearrangements of the molecules. The concept of $S_c(T)$ has been also used to discuss the glass transition in metallic glasses [26, 27]. On the other hand, a new interpretation to the CRR accompanied by the viscous flow has been proposed in the light of the BSCNF model [15]. According to this model, larger size of CRR in more fragile systems results from the preferential break of weaker parts of the bonds between the structural units. In this way, the view of the relaxation by the BSNCF model gives the same result as that described by the Adam-Gibbs theory, and provides an interpretation to the cooperativity from a different point of view. Based on

this standpoint, we emphasize that N_B could be a new indicator that quantifies the cooperativity which is accompanied by the viscous flow. The degree of cooperativity is evaluated by using a simple relation described by Eq. (5).

The relation between the exponent of the Kohlrausch-Williams-Watts (KWW) function β_{KWW} and the fragility index m is shown in Fig. 4. The values of β_{KWW} are calculated using the following relationship given by Vilgis; $D=(T_0/T_g)^2/(1-\beta_{KWW})^2$ [28]. The term T_0/T_g is calculated by using Eq. (3). Here, D is given by $D=B_{VFT}/T_0$ where B_{VFT} is one of the parameters of the VFT equation; $\ln \eta = \ln \eta_0 + B_{VFT}/(T-T_0)$. The Vilgis's relation connected with D, T_0, T_g, and B_{VFT} has been also used in the literature [11]. There, the relation has been used to check the value of the stretched exponent β_{KWW} of the BMG, $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$. Their result showed that in this BMG $\beta = 0.86$ [11]. The value obtained in our analysis for the same material is $\beta_{KWW} \approx 0.79$, which differs by certain amount. This difference is due to the different fitting parameters used in both analyses. However, we want to point out that, the behaviour shown in Fig. 4 reproduces the inverse correlation between β_{KWW} and the fragility index m, which is similar to the behaviour found empirically [18]. In addition, the result shown in Fig. 4 provides a sound physical basis to the stretched exponent. According to the BSCNF model, the cooperativity described by N_B can be correlated theoretically with the fragility index m. Smaller value of β_{KWW} means more spread relaxation time spectrum in the structural relaxation process [5]. That is, smaller value of β_{KWW} corresponds to larger degree of cooperativity and fragility, which are consistent to our results shown in Fig. 3 and Fig. 4.

4. Conclusions

In the present work, we discussed in the light of the Bond Strength – Coordination Number Fluctuation (BSCNF) model, the correlation between the fragility and the cooperativity in bulk metallic glass-forming liquids. It has been shown that the BSCNF model provides a new insight to understand the structural relaxation. More specifically, it was pointed out that the quantity N_B, which gives the number of structural units involved in the thermally activated viscous flow, could be a new indicator to analyze the viscosity and fragility of glass-forming liquids. It was also shown that the characteristic temperature ratio T_0/T_g, N_B, and the stretched exponent β_{KWW} of the KWW function, are mutually correlated through the fragility index m. By using the BSCNF model, it is expected that other fundamental quantities related to BMGs such as the elastic properties can be understood in terms of the cooperativity.

Acknowledgements

The author (M. Ikeda) thanks the financial support by Kumamoto University Global COE program, “Global Initiative Center for Pulsed Power Engineering”. This work was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19560014).

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Figure Captions

Fig. 1: The behaviors of the fragility index constant line described by Eq. (1) (broken line) and by Eq. (4) (solid curve). The following values for the viscosities were used, η_{Tg} $=10^{12}$ Pa·s and $\eta_0=10^{-5}$ Pa·s. The values of B^* and C^* are determined by the intersection between these two lines. With these values of B^* and C^*, the viscosity behavior described by the BSCNF model becomes identical to that described by the VFT equation.

Fig. 2: The characteristic temperature ratio T_0/T_g vs. the fragility index m in bulk metallic glass-forming liquids. The numbers indicate the metallic materials shown in Table 1. The data used are taken from the literatures [7-9]. The three curves drawn as a function of m are reproduced by Eq. (3).

Fig. 3: Relationship between N_B and the fragility index m. The values of N_B are calculated from Eq. (5). The symbols are the same to those used in Fig. 2.

Fig. 4: The behaviors of the stretched exponent of the KWW function β_{KWW} and the fragility index m calculated by using, $D=(T_0/T_g)^2/(1-\beta_{KWW})^2$ [28] and Eq. (3).

Table Caption

Table 1: Characteristic temperature ratio T_0/T_g, N_B, stretched exponent of the KWW function β_{KWW}, fragility index m, the value of $\ln(\eta_{Tg}/\eta_0)$, and the set of values (B^*,C^*) for eighteen bulk metallic glass-forming liquids. The data of the materials are taken from the works [7] (No.1 – No.9), [8] (No.10 – No.13), and [9] (No.14 – No.18). The values of $\ln(\eta_{Tg}/\eta_0)$ with * are originally given by $\ln(\tau_{Tg}/\tau_0)$. The viscosity η and the relaxation time τ are connected through the relation, $\tau=\eta/G_\infty$ [20], where, τ_{Tg} and τ_0 are the values of the relaxation time at T_g and at the high temperature limit, and G_∞ is the shear modulus at high frequency, respectively.

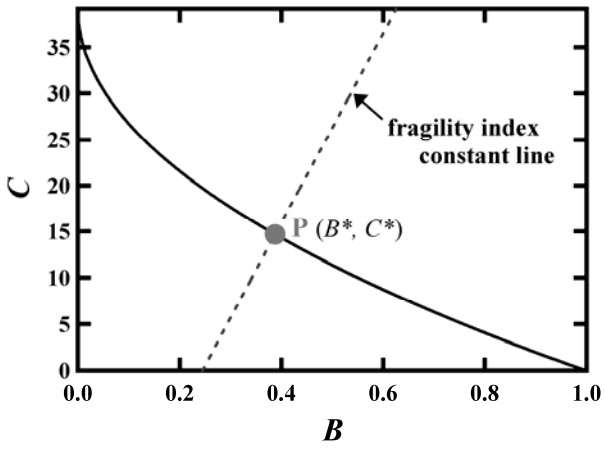
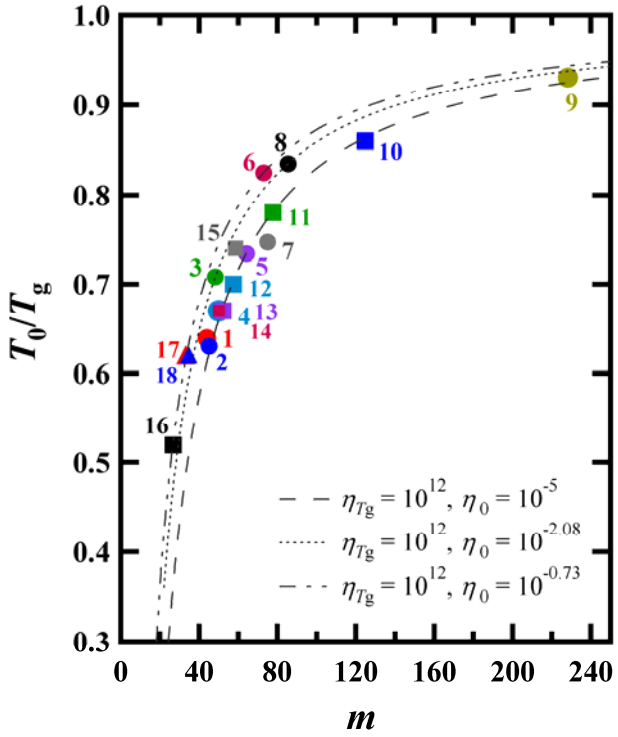

35
30
25
20
15
10
5
0
C
0.0
0.2
0.4
0.6
0.8
1.0
B
fragility index
constant line
P (B*, C*)

Fig. 1


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
T_0/T_g
0
40
80
120
160
200
240
m
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-5}$
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-2.08}$
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-0.73}$
1
2
3
4
5
6
7
8
9
10
11
12
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14
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16
17
18

Fig. 2

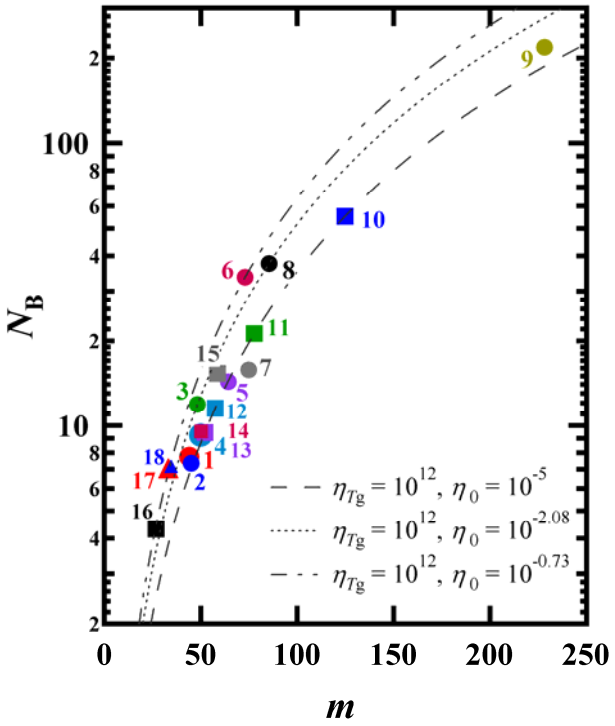
N_B
100
10
2
8
6
4
2
8
6
4
2
0
50
100
150
200
250
m
9
10
6
8
11
15
7
3
5
12
14
4
13
18
1
17
2
16
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-5}$
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-2.08}$
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Fig. 3

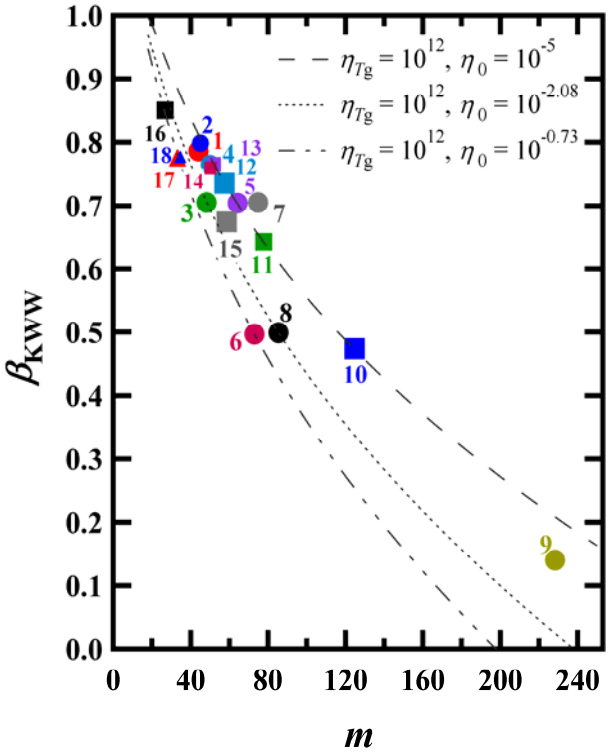
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-5}$
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-2.08}$
$\eta_{Tg} = 10^{12}$, $\eta_0 = 10^{-0.73}$
β_{KWW}
m
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
40
80
120
160
200
240
16
2
1
18
4
13
17
14
12
5
3
7
15
11
8
6
10
9

Fig. 4

No.	Material	T_0/T_g	N_B	β_{KWW}	m	$\ln(\eta_{Tg}/\eta_0)$	(B^*, C^*)	Ref.
1.	$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	0.64	7.8	0.79	44.0	36.51	(0.41, 13.1)	[7]
2.	$Mg_{65}Cu_{25}Y_{10}$	0.63	7.4	0.80	45.0	38.34	(0.37, 14.1)	
3.	$Pd_{48}Ni_{32}P_{20}$	0.71	12.0	0.71	48.2	32.32	(0.50, 9.3)	
4.	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	0.67	9.3	0.77	49.9	37.96	(0.45, 12.4)	
5.	$Pt_{60}Ni_{15}P_{25}$	0.73	14.3	0.70	64.2	39.25	(0.54, 10.3)	
6.	$Pd_{77.5}Cu_6Si_{16.5}$	0.83	33.7	0.50	73.0	29.32	(0.68, 5.0)	
7.	$Pd_{77}Cu_{6.5}Si_{16.5}$	0.75	15.8	0.71	74.9	43.64	(0.56, 10.9)	
8.	$Au_{76.9}Ge_{13.65}Si_{9.45}$	0.84	37.7	0.50	85.4	32.41	(0.70, 5.2)	
9.	$Al_{85}Ni_8Ce_7$	0.93	218.6	0.14	228.2	36.34	(0.87, 2.4)	
10.	$Ni_{65}Nb_{35}$	0.86	55.1	0.47	124.1	39.10 *	(0.75, 5.2)	[8]
11.	$Ni_{60}Nb_{35}Sn_5$	0.78	21.2	0.64	77.3	39.10 *	(0.61, 8.4)	
12.	$Ni_{57}Fe_3Nb_{35}Sn_5$	0.70	11.5	0.74	57.5	39.10 *	(0.50, 11.5)	
13.	$Ni_{60}(Nb_{40}Ta_{60})_{34}Sn_6$	0.67	9.5	0.77	51.9	39.10 *	(0.54, 12.7)	
14.	$Pd_{40}Ni_{40}P_{20}$	0.68	9.5	0.76	50.1	37.55	(0.46, 12.1)	[9]
15.	$Cu_{47}Ti_{34}Zr_{11}Ni_8$	0.74	15.4	0.67	58.6	34.68	(0.55, 8.8)	
16.	$La_{55}Al_{25}Ni_5Cu_{10}Co_5$	0.52	4.3	0.85	26.7	29.65	(0.27, 14.2)	
17.	$La_{55}Al_{25}Ni_5Cu_{15}$	0.62	7.1	0.77	33.3	28.97	(0.39, 10.9)	
18.	$La_{55}Al_{25}Ni_{20}$	0.63	7.2	0.78	34.7	29.98	(0.39, 11.2)	

Table 1