Development of Mo-Ni-Si-B metallic glass with high thermal stability and H versus E ratios

Jinwoo Kim ^a, Joon Seok Kyeong ^b, Moon-Ho Ham ^c, Andrew M. Minor ^{d,e}, Do Hyang Kim ^f,
Eun Soo Park ^{a,*}

^a Research Institute of Advanced Materials, Department of Materials Science and Engineering,
Seoul National University, Seoul 08826, Republic of Korea

^b Materials Research Team, R&D Division, Hyundai Mobis, Yongin, Gyeonggi-do 16891 Republic of
Korea

^c School of Materials Science and Engineering, Gwangju Institute of Science and Technology,
Gwangju 61005, Republic of Korea

^d Department of Materials Science and Engineering, University of California, Berkeley, CA 94709,
USA

^e National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA
94720, USA

^f Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Republic of
Korea

* Corresponding author. Tel.: +82 2 880 7221; fax: +82 2 885 9671.

Email address: espark@snu.ac.kr (E.S. Park)

Abstract

We report a novel Mo-Ni-Si-B metallic glass which can be solidified into fully amorphous state by melt-spinning process, with high crystallization onset temperature of over 1100 K, extremely high Vickers hardness of 27.5 ± 2.2 GPa and relatively low Young's modulus of 364.3 ± 6.6 GPa. The dense cluster-packing model suggests that the addition of boron up to 10 at.% can occupy vacant cluster-interstices of (Mo, Ni)-Si cluster arrays, which results in a more efficiently dense-packed cluster structure, destabilizes the formation of nanocrystalline phases, and systematically increases the glass-forming ability (GFA) in Mo-Ni-Si-B alloys. The GFA parameters that do not directly rely on T_g , such as ΔT^* and ε parameter, show greater reliability to evaluate GFA for Mo-Ni-Si-B metallic glass exhibiting no clear T_g . The H/E and $H^2/(2E)$ ratios of the newly developed Mo-Ni-Si-B metallic glass, which reflect wear resistance and resilience, exhibit the highest values among various hard ceramic materials as well as metallic glass-forming alloys developed up to now. These advantages of Mo-Ni-Si-B metallic glass can be used more widely to form a high temperature wear-resistant coating layer on various substrates. Furthermore, the same idea might be used to form a metallic glass-nitride nanocomposite coating layer by reactive deposition in N_2 ambient, with highly lubricative property and high wear-resistance, especially at high temperature.

Keywords

Molybdenum, Metallic glass, Glass-forming ability, H versus E ratio, Wear resistance

1. Introduction

Metallic glasses have excellent mechanical properties, such as high strength, hardness, large elastic strain limit and low elastic modulus [1-3], and thus are expected to endure extremely harsh environments required in modern industries. However, metallic glasses show limited thermal stability against crystallization, and they lose their unique mechanical properties at high temperature over a crystallization onset temperature (T_x). The drawback of low thermal stability of the metallic glasses has limited their applications as structural materials at high temperature.

In this regard, efforts to develop thermally stable metallic glasses continued for a few decades. The metallic glasses based on the early transition metal (ETM) elements such as Zr and Ti, which are widely used for composing glass-forming systems, have relatively low thermal stability with T_x under 800 K despite their high glass-forming ability (GFA) [4, 5]. The late transition metal (LTM)-based metallic glasses such as Ni-, Co- and Fe-based alloys have improved thermal stability compared to the ETM-based metallic glasses, but generally they exhibit T_x under 1000 K [6-11]. However, the metallic glasses based on refractory metal elements, such as Mo, W, Ta and Nb, tend to have high T_x because T_x of metallic glasses approximately scales with their liquidus temperature (T_l) [12]. A few refractory metal based-systems have been reported [12-16] to form amorphous phases with high T_x over 1000 K and exceptional mechanical properties inherited from their base elements, while most of them have low GFA limiting them to be fabricated only through mechanical alloying process due to their high T_l , ironically.

High-temperature wear-resistant coatings have been widely used for materials under continuous frictional stress without extra cooling process, such as high-speed bearings, cutting tools and engines, and also have been continuously developed to endure extreme environments required in modern mechanical engineering technologies

and industries. Although high hardness (H) has been regarded as a primary property for highly wear-resistant coating materials, a relatively low elastic modulus (e.g. Young's modulus, E) is also required for achieving high wear resistance with reasonable reliability by reducing elastic property mismatch between coating and substrate and by increasing elastic strain to failure which is related to the H/E ratio [17, 18]. A hard material generally demonstrates a high elastic modulus. However, due to the absence of long-range atomic order and dislocation-mediated slip, metallic glasses show high yield stress and hardness close to the theoretical limit, while the elastic moduli of metallic glasses are macroscopically much lower than their crystalline counterparts [3]. From the combination of high hardness and low elastic modulus, metallic glasses are favorable to have high durability against frictional stress. Thus, by enhancing their thermal stability against relaxation and crystallization, metallic glasses can be widely applied as wear-resistant coating materials, even at high temperature.

In this article, we report a novel Mo-Ni-Si-B metallic glass which can be fabricated by melt-spinning process, with high thermal stability of $T_x = 1112$ K, extremely high Vickers hardness of 27.5 ± 2.2 GPa and relatively low Young's modulus of 364.3 ± 6.6 GPa. In order to enhance the GFA of Mo-Ni-Si ternary system, boron was selected as the fourth alloying element. The effect of boron addition to the Mo-Ni-Si system, $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($x = 0, 2, 5, 7, 10$), on GFA and mechanical properties of as-spun ribbons was systematically evaluated using transmission electron microscopy (TEM) and nanoindentation tests. Furthermore, we fabricated thin film metallic glass using the developed $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ glass-forming alloy, which exhibits properties similar to fully amorphous ribbon samples. The dense cluster-packing model [19] was adopted to predict the atomic configurations of the Mo-Ni-Si-B metallic glass and various GFA parameters were applied to describe GFA of the newly developed Mo-Ni-Si-B

metallic glass with no clear T_g . Indeed, the H/E [17, 20] and $H^2/(2E)$ [21] ratios of the newly developed Mo-Ni-Si-B metallic glass were compared with those of various metallic glass-forming alloys and hard ceramic materials to evaluate the potential of the Mo-Ni-Si-B metallic glass as a high temperature wear-resistant coating material.

2. Experimental

($\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$) $_{100-x}\text{B}_x$ ($x = 0, 2, 5, 7, 10$) alloy ingots were prepared by arc-melting with high-purity elements of Mo (99.5%), Ni (99.995%), Si (99.9%), and B (99.5%), under Ti-gettered argon atmosphere. Rapidly solidified ribbons were prepared by melt-spinning process. The alloy ingots were re-melted in quartz tube by induction heater, and ejected with an over-pressure of 50 kPa through a 0.5 mm-diameter circular nozzle onto a copper wheel rotating with a surface velocity of 40 m/s. Thin film samples were prepared on flat stainless steel substrates (Type 304 SS) by an e-beam evaporator (SNTEK Co. Ltd) using the ($\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$) $_{90}\text{B}_{10}$ alloy ingot with a deposition rate of 1 Å/s. The film thickness was measured by a surface profiler (Bruker Dektak XT). The final thickness of the as-deposited film was around 100 nm.

The structures of the samples were confirmed by X-ray diffraction (XRD: Rigaku CN2301) for the as-spun ribbon samples and grazing incidence X-ray diffraction (GI-XRD: Bruker D8 Advance) for the thin film sample, using monochromatic Cu K α radiation. The crystallization behaviors of the as-cast ribbons were investigated by differential scanning calorimetry (DSC: Mettler Toledo TGA/DSC 1) at a heating rate of 20 K/min. The microstructures of the samples were examined by TEM (Jeol JEM-3010, Philips CM300FEG/UT) operated at 300 kV. The thin foil TEM specimens were prepared by ion milling (Gatan 695 PIPS II) with liquid nitrogen cooling after mechanical thinning process. In order to reduce ion-milling time and re-deposition effect, the ribbon samples

were mechanically polished to a wedge shape with a wedge angle of 1° (Allied Multiprep polishing system) before ion-milling.

The mechanical properties of the ribbon samples and the thin film sample were evaluated from instrumented nanoindentation tests. The nanoindentation tests were performed for the ribbon samples using a nanomechanical tester (Hysitron TI 750 TriboIndenter) and for the thin film sample using in-situ SEM indentation tester (Hysitron PI-85 SEM Picoindenter) for precise measurements in small indentation depth conditions. Indenting force was loaded up to peak force in 5 s with constant loading rate using Berkovich diamond tip, remained at the peak force for 2 s, and then was unloaded in 5 s. The peak force was 5 mN for the tests of the ribbon samples and the hardness measurement of the thin film. For Young's modulus estimation of the thin film, the peak forces of serial indentation tests were in the range of $200 \sim 5000 \mu\text{N}$. The Vickers microhardness of the selected sample was also measured with 0.1 kgf load condition by the microhardness tester (EMCO-TEST DuraScan 70). Both the nanoindentation and microhardness tests were repeated 10 times to obtain average values, and standard deviations were used as error ranges.

3. Results

Since the liquidus projection and eutectic point of the Mo-Ni-Si ternary phase diagram have not been reported yet, the GFA variation in the ternary system was firstly investigated by experimental process. Although we could not find a glass-forming composition area in the Mo-Ni-Si ternary system, relatively broad peaks were observed in XRD patterns of the $\text{Mo}_{100-i-j}\text{Ni}_i\text{Si}_j$ as-spun ribbons with the composition range of $40 \leq i \leq 60$, $0 \leq j \leq 20$. In particular, at the composition of $\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$, wide peak

broadening which is related to nanocrystallization during solidification appears at two-theta range of 40 – 47° as shown in Figure 1, indicating that the alloy exhibits relatively high liquid stability (= low T_l). As marked in Figure 1, the $\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$ ternary alloy has crystalline peaks which originate from nanocrystalline phases of $\text{Mo}_{24}\text{Ni}_{21}\text{Si}_7$ (ICDD PDF No. 01-089-5106, $\text{Mo}_6\text{Ni}_{5.25}\text{Si}_{1.75}$) and $\text{Mo}_{31}\text{Ni}_{19}$ (ICDD PDF No. 00-047-1129, $\text{Mo}_{1.24}\text{Ni}_{0.76}$). Then, the effect of boron as a fourth element on the structure and GFA was investigated in $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($x = 0, 2, 5, 7, 10$) alloy. As shown in Figure 1, the intensities of these sharp crystalline peaks clearly become lower with increasing boron contents, and the broad diffuse peak without clear crystalline peak in the range of 40~47° starts to appear with the addition of boron over 7 at.%, while a small $\text{Mo}_{24}\text{Ni}_{21}\text{Si}_7$ peak at near 37° still remains. With further addition of boron, $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ shows a sole broad diffuse peak without any crystalline peaks, as a typical pattern of fully amorphous materials.

Figure 2 shows a DSC thermogram of as-spun Mo-Ni-Si-B alloy ribbons. $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{95}\text{B}_5$ or the other samples with under 5 at.% of boron exhibit no clear characteristic transformation behavior of amorphous phase before melting. In contrast, $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{93}\text{B}_7$ and $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ show clear exothermic peaks which correspond to crystallization reactions of the amorphous phase. The crystallization onset temperatures (T_x) of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{93}\text{B}_7$ and $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ were 1098 K and 1112 K, respectively, which are significantly higher than those of general transition metal-based glass-forming alloys such as Cu-, Zr-, Ni-, and Fe-based systems. $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{93}\text{B}_7$ has lower enthalpy change of crystallization (20.4 J/g) compared to $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ (33.1 J/g) because of partially crystallized structure and low fraction of the amorphous phase in $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{93}\text{B}_7$ as shown in XRD patterns.

The microstructures of the as-spun ribbons were carefully investigated by TEM.

The bright-field (BF) images and selective area diffraction patterns (SADPs) of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($x = 0, 2, 5, 7, 10$) ribbons are shown in Figure 3. From $x = 0$ to 5 samples, fully nanocrystalline phases were formed in as-spun state, and the spot patterns from multiple nanograins of different orientations create ring-type patterns with irregular intensity variation, as shown in Figure 3 (a-c). Furthermore, the SADPs of as-spun ribbons were converted to diffraction profiles by azimuthal integration [22] as shown in insets of Figure 3 (a-e), which correspond to the XRD patterns of Figure 1. The relatively sharp peaks from nanocrystalline phases appear in the diffraction profile of $\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$ ternary alloy, while the peaks clearly broaden and profile intensities decrease with the addition of boron. The average grain sizes of the samples with $x = 0, 2$, and 5 were 63 nm, 43 nm, and 26 nm, respectively, which shows that the grain size of nanocrystalline samples decreases with increasing boron content (Figure 3 (f-h)). With boron addition over 7 at.%, amorphous matrix was formed with embedded crystalline phases of the average sizes under 10 nm (Figure 3 (i)). In $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ sample, the homogeneous amorphous structure was confirmed by uniform contrast in the BF image of Figure 3 (j) and the broad diffuse halo ring pattern in Figure 3 (e). The random atomic arrangement in the high-resolution image and the broad ring pattern without any diffracted spot in the inset fast Fourier transformed (FFT) pattern of Figure 4 also demonstrate the fully amorphous structure of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ sample.

Figure 5 shows nanohardnesses and reduced elastic moduli (E') of the $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($0 \leq x \leq 10$) as-spun ribbons evaluated by nanoindentation test. The nanohardness values of the as-spun samples were over 20 GPa, which are much higher than that of nanocrystalline Mo (9.98 GPa [23]). The inset of Figure 5 shows grain size (D) variation depending on boron content (X_B) and its exponential fitting line. The relation between grain size and nanohardness (H) is also fitted with Hall-Petch relation

($H = H_0 + k_H D^{-0.5}$) [24-26] and the obtained parameters for $x = 0, 2$ and 5 alloys are $H_0 = 19.65$ GPa and $k_H = 9.03$ GPa·nm^{1/2}. The high H_0 value means that the exceptional hardness of nanocrystalline Mo-Ni-Si-B originates from inherent bond nature of the alloy. From X_B - D and D - H relations, the hardness variation of fully nanocrystalline samples ($x = 0$ to 5) is well fitted with Hall-Petch relationship as shown in Figure 5. Interestingly, with formation of amorphous phase, the nanohardness values of (Mo₄₅Ni₄₅Si₁₀)₉₃B₇ and (Mo₄₅Ni₄₅Si₁₀)₉₀B₁₀ ribbons increased drastically as compared with the fully nanocrystalline samples ($x = 0$ to 5), and the nanohardness of fully amorphous (Mo₄₅Ni₄₅Si₁₀)₉₀B₁₀ ribbon was 24.6 ± 0.4 GPa. Furthermore, the average Vickers hardness value from the measurements repeated 10 times was 27.5 ± 2.2 GPa, which is comparable with nanohardness value.

From instrumented nanoindentation test, the Young's modulus (E) of a sample is determined using the relation [27]

$$\frac{1}{E^*} = \frac{1}{E'} + \frac{1}{E'_i} \quad (1)$$

where the superscript (') denotes,

$$E' = \frac{E}{1-\nu^2} \quad (2)$$

E^* is the "specimen and indenter" modulus, which can be directly obtained from a nanoindentation result using the unloading part of load-displacement curve and the projected area of the elastic contact. ν is Poisson's ratio, and the subscript i denotes indenter tip, where $E_i = 1141$ GPa and $\nu_i = 0.07$ for diamond tip [28]. E' is reduced elastic modulus which represents the mean value of elastic modulus in the indented zone [29]. Figure 5 also shows reduced elastic moduli of the (Mo₄₅Ni₄₅Si₁₀)_{100-x}B_x ($0 \leq x \leq 10$) as-

spun ribbons obtained from nanoindentation test. E' of the fully nanocrystalline samples increased with the addition of boron or decrease in grain sizes (=increase in hardness), while the formation of amorphous phase does not lead to a meaningful increase in E' despite drastic increase of nanohardness in $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{93}\text{B}_7$ and $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloys. The Young's modulus of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ metallic glass is 364.3 ± 6.6 GPa which is obtained by conversion from reduced elastic modulus ($E' = 407.6$ GPa) under the assumption of $0.3 < \nu < 0.35$.

A thin film sample was deposited using $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloy ingot as a source of e-beam evaporation process. The final thickness of the as-deposited film was around 100 nm. The GI-XRD pattern of the as-deposited film (Figure 6) includes a broad diffuse peak of an amorphous phase and a few sharp peaks from the stainless steel substrate underneath the thin film.

In order to measure mechanical properties such as hardness and elastic modulus only from a thin film directly, the indentation depth is limited to less than 1/10 of the film thickness [30]. The indentation with a depth under 10 nm does not give reliable measurement results due to instrumental limitation, so it is difficult to directly measure hardness of the 100 nm-thick film deposited from $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloy. Instead, the nanohardness of the composite (film and substrate) and the raw substrate was measured from indentation to a depth over film thickness. Then, the film nanohardness is estimated using the relation from the Jönsson and Hogmark model [31],

$$H_f = H_s + (H_c - H_s) / \left\{ 2 \frac{Ct}{h} - \left(\frac{Ct}{h} \right)^2 \right\}, \quad (3)$$

where H_f , H_s , and H_c are the hardness of the film, the substrate and the composite, respectively. h is indentation depth (= 130 nm) and t is the film thickness (= 100 nm). C is a geometric constant determined from the semi-apical angle (δ) of indenter tip. For

the Berkovich tip ($\delta = 65.3^\circ$), C is equal to $1 - \sin \delta$ ($= 0.0915$) for a hard brittle film on a soft substrate, and $\cos^2 \delta$ ($= 0.1746$) for a plastically deformable film on a hard substrate [32]. Considering the Mo-Ni-Si-B amorphous film as the former case, the estimated nanohardness of the film using the Jönsson and Hogmark model is 28.7 ± 3.77 GPa which is close to the measured value of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ as-spun ribbon. The measured nanohardness of the substrate and the composite and the estimated nanohardness of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ amorphous film are also listed in Table 1.

Due to the same instrumental limitation of thin film indentation test, the Young's modulus of the deposited Mo-Ni-Si-B thin film was estimated by serial nanoindentation tests with various indentation depths. Figure 7 shows the reduced elastic moduli of the composite ($E_c' = (1/E^* - 1/E_f')^{-1}$ from equation (1)) depending on a/t values obtained from different indentation depths. a is the characteristic size of the contact area, which is $a \approx 2.8 h_c$ for Berkovich tip, where h_c is the contact depth of indentation [29]. The reduced elastic modulus of the film (E_f') can be estimated from an empirical relationship proposed by Doerner and Nix [33, 34]

$$\frac{1}{E_c'} = \frac{1}{E_f'} + \left(\frac{1}{E_s'} - \frac{1}{E_f'} \right) e^{-\alpha(t/a)}, \quad (4)$$

where α is an empirical constant, and the subscripts c, f and s denote composite, film and substrate, respectively. The red line of Figure 7 shows a fitting curve using Doerner and Nix function with $\alpha = 1.83$ and the estimated E' of Mo-Ni-Si-B thin film (E_f') is 400.0 ± 10.1 GPa ($E_f = 357.5 \pm 6.5$ GPa) under the assumption of $0.3 < \nu < 0.35$, which is comparable with that of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ amorphous ribbon ($E'_{\text{ribbon}} = 407.6 \pm 10.9$ GPa and $E_{\text{ribbon}} = 364.3 \pm 6.6$ GPa).

4. Discussion

4.1. Glass formation in Mo-Ni-Si-B metallic glass

The GFA of refractory metal (including molybdenum)-based system is limited due to the high melting temperature of refractory metals and eutectic reactions at high temperature in refractory alloy systems [16]. The empirical rules for GFA include (1) multicomponent system consisting of more than three elements, (2) significant atomic size mismatch over 12 % and (3) large negative heat of mixing relations among constituent elements [1]. From large negative heat of mixing relations, the deep eutectic reaction at low temperature is favorable for achieving high GFA. Among the binary systems of Mo with other transition metal elements such as Fe, Co, Ni, Zr and Hf which have eutectic reaction, the lowest eutectic point appears in Mo-Ni system at 1590 K, $\text{Mo}_{35.8}\text{Ni}_{64.2}$ composition [35]. In order to find a composition with high GFA and higher Mo atomic fraction than eutectic composition of Mo-Ni, Si was added due to its large negative heat of mixing relation [36] with both Mo and Ni (Figure 8) and the existence of eutectic point at higher contents of Mo, 2293 K of $\text{Mo}_{73.6}\text{Si}_{26.4}$ composition and 2173 K of $\text{Mo}_{46}\text{Si}_{54}$ composition [37]. The liquidus projection and eutectic point of Mo-Ni-Si ternary phase diagram have not been reported previously, so the GFA variation in the ternary system was systematically investigated through experimental process. The result shows that nanocrystallization occurs during solidification in the $\text{Mo}_{100-i-j}\text{Ni}_i\text{Si}_j$ ($40 \leq i \leq 60, 0 \leq j \leq 20$) as-spun ribbons, thus indicating that the alloys have larger undercooling (ΔT) which leads to higher homogeneous nucleation rate ($N_{\text{homo}} \propto \exp(-1/(\Delta T/T_m)^2)$) and lower growth rate. In particular, at near the composition of $\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$, wide peak broadening appears in two-theta range of $40 - 47^\circ$ as shown in Figure 1, which means the formation of fine nanocrystalline phases down to 100 nm as

shown in Figure 3 (f).

In order to enhance GFA of Mo-Ni-Si alloy system, boron was chosen as an additional alloying element, because boron has large negative heat of mixing relation and also large atomic size difference over minimum 30 % with the other three elements (Figure 8). Chemical mixing enthalpy of an alloy based on the extended regular solution model ($\Delta H^{chem} = \sum \Omega_{ij} c_i c_j$) can be calculated with the regular solution interaction parameter ($\Omega_{ij} = 4 \times \Delta H_{ij}^{mix}$) [38]. ΔH^{chem} of $\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$ alloy is -19.2 kJ/mol and decreases with the addition of boron to -25.4 kJ/mol for $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$. The effect of atomic size difference in an alloy can be estimated by normalized mismatch entropy (S_σ/k_B , where k_B is the Boltzmann constant) [38], and S_σ/k_B increases with the addition of small boron atoms, from 0.139 for $\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10}$ to 0.404 for $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$. The tendency for the variation of ΔH^{chem} and S_σ/k_B shows that the addition of boron to Mo-Ni-Si stabilizes an amorphous phase against corresponding crystalline phases. In accordance with the estimation of ΔH^{chem} and S_σ/k_B , Figures 1-4 clearly show the dependence of GFA on the amount of boron addition. With increasing B contents the grain size in as-spun ribbon decreases and an amorphous phase starts to form with addition of boron over 7 at.%, and then $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ forms a fully amorphous ribbon.

In order to explain how the boron addition enhances the GFA of the alloys, the atomic structure of amorphous Mo-Ni-Si-B alloys was predicted using the dense cluster-packing model suggested by Miracle [19]. The model involves efficiently packed solute-centered atomic clusters. The primary cluster-forming solute α forms the primary clusters with surrounding solvent atoms Ω , and the coordination number (N_α) depends on the atomic size ratio ($R_\alpha = r_\alpha/r_\Omega$ where r is atomic radius) [39]. An FCC-type dense

packing array of the primary clusters composes an idealized cluster unit cell, and additional solutes β and γ occupy cluster-octahedral and cluster-tetrahedral interstices, respectively. The coordination number (N_β, N_γ) of each solute also depends on the atomic size ratio with solvent atom ($R_\beta = r_\beta/r_\Omega, R_\gamma = r_\gamma/r_\Omega$), and the predicted atomic structure models can be designated as $\langle N_\alpha - N_\beta - N_\gamma \rangle$ with the coordination number of solutes.

This model is potentially based upon a premise that glass-forming alloys have a single major element whose composition is far above 50 at.%, but the Mo-Ni-Si-B alloys developed in this study have dual major elements of Mo and Ni with equivalent concentration (> 40 at.%) and similar atomic radius within 8 % difference. In order to adapt this model to the developed alloy system, an assumption is introduced that both Mo and Ni act as a major solvent element from the equivalent composition and relatively small atomic size difference. By regarding both transition metals (Mo, Ni) as solvent atoms, their average atomic radius can be taken as the atomic radius of solvent ($r_{Mo} = 1.39 \text{ \AA}$, $r_{Ni} = 1.28 \text{ \AA}$ [40], $r_{avg, solvent} = (r_{Mo} + r_{Ni})/2 = 1.335 \text{ \AA}$). From atomic radius values ($r_{Si} = 1.02 \text{ \AA}$, $r_B = 0.78 \text{ \AA}$ [40]), the atomic size ratios of solutes Si and B (R_{Si} , R_B) were 0.764 and 0.584, which correspond to the calculated coordination numbers [39] of 9.60 and 7.67, respectively. Taking the theoretical coordination numbers as integers, the predicted dense cluster-packing model of (Mo, Ni)-Si-B system is rationalized as $\langle 10-8 \rangle$ model with vacant γ position. The $\langle 10-8 \rangle$ γ vacant model was reported to provide a good prediction on alloy composition of commercial Metglas as well as Fe-(Si, P)-(B, C) glass-forming systems [19].

Figure 9 shows the comparison of relative atomic size ratios ($R_\alpha = r_{solute}/r_{solvent}$) and compositions for $(Mo_{45}Ni_{45}Si_{10})_{100-x}B_x$ ($x = 0, 2, 5, 7, 10$) and the glass-forming composition range of Fe-metalloid (Fe-(Si, P)-(B, C)) metallic glasses [41-44] with prediction as $\langle 10-8 \rangle$ γ vacant model. The ideal composition of $\langle 10-8 \rangle$ γ vacant model is

marked as the red solid circles and the glass-forming composition range of Fe-(Si, P)-(B, C) system with melt spinning technique is expressed with the purple vertical line in Figure 9. The atomic ratios of (Si, P) and (B, C) to solvent Fe in Fe-(Si, P)-(B, C) system are 0.797 and 0.609, respectively, which are very close to the ideal atomic ratios for the coordination number 10 and 8 ($R_{N=10} = 0.799$, $R_{N=8} = 0.617$). As shown in Figure 9, the glass-forming range of Fe-(Si, P)-(B, C) system exists near the ideal composition of <10-8> γ vacant model, and this accordance shows that the dense cluster-packing model provides a good prediction on the favorable alloy compositions for glass formation in Fe-(Si, P)-(B, C) system [19]. Similarly, the predicted dense cluster-packing model of Mo-Ni-Si-B system with the assumption of dual solvent atoms (Mo, Ni) is also <10-8> γ vacant model, and the solute atomic size ratios and compositions for $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($x = 0, 2, 5, 7, 10$) are marked as the solid diamonds in Figure 9. With increasing B addition in $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ alloys, the alloy composition approaches the ideal composition in <10-8> γ vacant model. This means, according to the ideal dense cluster-packing model, the addition of boron can occupy vacant cluster-interstices of (Mo, Ni)-Si cluster arrays, which results in more densely packed cluster structure. The slight difference in composition between $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ and ideal <10-8> γ vacant model can be due to difference of atomic size ratios of Mo-Ni-Si-B system from the ideal ratio values for coordination numbers of 10 and 8, or the influence of pronounced covalent interatomic bonding of metalloid atoms [45]. As suggested by Figures 1-3, the GFA of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ alloys clearly increases with the addition of B and as the alloy composition approaches the ideal composition in <10-8> γ vacant model. Considering this, the <10-8> γ vacant model shows a good agreement with the favorable composition for glass formation in Mo-Ni-Si-B alloy system, suggesting that the addition of boron results in more efficiently packed atomic structure, destabilizes the formation of nanocrystalline phases, and increases the GFA of the alloy [41].

The glass-forming alloy system can be categorized depending on the alloy components following Inoue's classification [1]. Figure 10 shows the classification diagram with five glass-forming alloy system groups slightly modified from reference [1]. The group I and group IV include metal-metalloid alloys represented by (Fe, Co)-metalloid and noble metal (Pt, Pd)-metalloid-type metallic glass. The distinctive feature of both systems is that the major element is LTM and generally the good glass-former alloys have the composition ratio of (metal : metalloid) near 80 : 20 [42]. Similarly, Mo-Ni-Si-B system has high GFA near the composition with transition metal (Mo, Ni)-metalloid (Si, B) ratio near 80 : 20 (for $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloy, metal : metalloid = 81 : 19), although it has an ETM element as one of major elements. From these aspects, the newly developed Mo-Ni-Si-B glass-forming alloy system can be categorized as a distinctive alloy system of group I.

To describe GFA in various alloys, many GFA parameters have been proposed on the basis of the characteristic transformation temperatures of metallic glasses such as T_g = glass transition temperature, T_x = crystallization onset temperature, T_l = liquidus temperature, and $T_m^{mix} = \sum X_i \cdot T_m^i$ with X_i and T_m^i being mole fraction and melting point, respectively, of the component i in a multi-component alloy [46-53]. Most of the parameters directly include T_g , for example $\gamma = \frac{T_x}{T_g + T_l}$ [50], except ΔT^* [47], α [53], T_{rx} [52], and $\varepsilon = \frac{\Delta T_m + \Delta T_x + T_x}{T_m^{mix}}$ parameter (here, $\Delta T_m = T_m^{mix} - T_m$, $\Delta T_x = T_x - T_g$) [51]. However, directly including T_g in the GFA parameter can cause some vagueness in evaluating the GFA [51] and the GFA parameters would significantly differ from real GFA in case of metallic glasses with no clear T_g , although it can be approximately calculated under the assumption of $T_g = T_x$. For the $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ metallic glass, the calculated γ parameter was 0.389 (if T_x is used instead of T_g), which is related to the estimated maximum section thickness (Z_{max}) and critical cooling rate (R_c) with $Z_{max, \gamma} = 3.05$ mm and

$R_c, \gamma = 86$ K/s [50]. These values do not give a satisfactory correlation with the real GFA of Mo-Ni-Si-B metallic glass ($Z_{max, exp.} =$ a few tens of micrometer), although it is possible to reduce GFA due to unique local atomic cluster structure similar with Fe-based metallic glasses consisting mainly of Fe and B [42]. On the other hand, the calculated ΔT^* parameter was 0.23, which is larger than 0.20 for most of metallic glass formers by melt-quenching in typical thicknesses (i.e., > 20 μm) at a cooling rate of 10^5 - 10^7 K/s [47]. The calculated ε was 0.718, which is related to $Z_{max, \varepsilon} = 1.54$ mm and $R_{c, \varepsilon} = 624$ K/s [51]. Although $Z_{max, \varepsilon}$ exhibits a higher value than $Z_{max, exp.}$, the ε parameter shows greater reliability for $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ metallic glass with no clear T_g .

4.2. H versus E relationship in Mo-Ni-Si-B metallic glass

Low thermal stability (or low T_x) is one of the main drawbacks which limit wide industrial applications of metallic glasses. A few LTM (Ni, Fe, Co)-based metallic glasses have crystallization temperatures near 1000 K, as listed in Table 2, while T_x over 1000 K can be obtained only in a few refractory metal (Mo, W, Ta ..)-based metallic glasses. Among the refractory metal-based systems, only a few alloys have GFA high enough to be fabricated to fully amorphous state even in ribbon-type samples (a few tens of micrometer thickness), and the others can be fabricated to amorphous state only by mechanical alloying, which may exhibit greater maximum departure from the equilibrium than rapid solidification process. However, $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ has relatively high GFA to form fully amorphous ribbon, and also has high thermal stability of $T_x = 1112$ K measured by DSC (Figure 2). This novel alloy system does not include a precious metal such as Ru, the rare transition metal belonging to the platinum group, so it is more economical than W-Ru-B system [12].

Furthermore, the amorphous $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloy shows extremely high hardness (27.5 ± 2.2 GPa in Vickers hardness), similar to hard ceramic materials (VC: 28.4 GPa, W_2B_5 : 26.5 GPa, SiC: 25.5 GPa, TiN: 20.6 GPa in Vickers hardness [54]), while the Young's modulus of the alloy (364.3 ± 6.6 GPa) is much lower than those of hard ceramic materials (VC: 430 GPa, W_2B_5 : 770 GPa, SiC: 480 GPa, TiN: 590 GPa [54]). Despite its excellent mechanical properties, $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ metallic glass is difficult to fabricate over ribbon scale (a few tens of micrometer thickness) to bulk scale (over 1 mm) due to relatively low GFA. To be free from the constraint of the feature, the novel Mo-Ni-Si-B metallic glass-forming system can be used as a surface coating material with good wear resistance as well as high thermal stability. It is confirmed that amorphous thin film exhibiting similar mechanical properties with metallic glass ribbon can be fabricated by e-beam evaporation process using $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloy, as shown in the GI-XRD result of Figure 6, the nanohardness of Table 1 and the elastic modulus of Figure 7. The small difference in hardness and elastic modulus between the thin film and the as-spun ribbon originates from the error of the estimation model and a slight chemical composition shift due to evaporation rate difference among the components during deposition process.

Based on these considerations, the possibility for a promising high temperature wear resistant coating material was evaluated by H/E and $H^2/(2E)$ parameters. High elastic moduli of hard ceramic coating materials well over 400 GPa cause extreme elastic property mismatch between coating and substrate [17], which results in significantly decreased durability of coating despite their high hardness. On the other hand, relatively low elastic modulus combined with high hardness of metallic glasses [1-3] is favorable for high wear-resistance and durability of coating materials. H/E ratio is a reliable indicator for evaluating wear resistance of coating materials, which is related to the elastic strain to failure [17, 20]. The $H^2/(2E)$ parameter is related to resilience of coating

material [21], which is analogous with $\sigma_y^2/(2E)$ for bulk materials. Figure 11 shows H/E and $H^2/(2E)$ values of various metallic glasses according to their T_x . The Vickers hardness and the Young's modulus values of the metallic glasses except Mo-Ni-Si-B alloy were taken from reference [55]. H/E ratios do not show a clear relationship with T_x , as shown in Figure 11 (a). Among the alloys marked in Figure 11 (a), Mo-Ni-Si-B metallic glass has much higher H/E ratio (0.075) than other glass-forming alloys and hard ceramic materials such as VC, W_2B_5 , SiC, and TiN (0.066, 0.035, 0.053, and 0.035, respectively, calculated from the data of [54]). On the other hand, $H^2/(2E)$ parameter has a clear tendency to increase with T_x , and Mo-Ni-Si-B metallic glass has largest $H^2/(2E)$ value over 1.0, far above the values of the other metallic glasses, as shown in Figure 11 (b). Thus, the novel Mo-Ni-Si-B metallic glass is expected to have excellent wear resistance and high capability for elastic energy absorption among glass-forming alloy systems, which make it a promising high temperature wear resistant coating material.

In addition, a combination of nitride-forming transition metal and transition metal with low elastic modulus (e.g., MoN-Cu [56]) provides an effective route to achieve high hardness and low elastic modulus (high H/E ratio) of a coating material [18]. Instead of the transition metal, a combination of hard nitride and metallic glass with relatively high hardness and low elastic modulus can be a promising route to design a good wear resistant coating material. If the reactive deposition technique such as reactive sputtering in N_2 ambient is used for the fabrication of a thin film from Mo-Ni-Si-B alloy, the deposited coating has a great possibility to form a multi-functional nanocomposite coating layer with nanoscale nitride phases (MoN, Si_3N_4) and metallic glass matrix due to high nitrifying ability of Mo [57] and high GFA of Mo-Ni-Si-B alloy. Therefore, it is possible to tailor hardness and elastic modulus and form a gradient thin film microstructure by reactive deposition of Mo-Ni-Si-B alloy in N_2 ambient to optimize the tribological property in a wide service temperature range, especially high

temperature regime.

5. Conclusions

A novel Mo-Ni-Si-B metallic glass was developed, which can be solidified into a fully amorphous ribbon by conventional melt-spinning process at $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ composition. The dense cluster-packing model suggests that Mo-Ni-Si-B metallic glass is supposed to have <10-8> cluster with vacant γ position, which is an atomic configuration similar to that of Fe-metalloid-type metallic glasses in metal-metalloid glass-forming group (Group I). The addition of boron can occupy vacant cluster-interstices of (Mo, Ni)-Si cluster arrays, which results in a more efficiently dense-packed cluster structure, destabilizes the formation of nanocrystalline phases, and increases the GFA of the alloy. Although $Z_{\max, \varepsilon} = 1.54$ mm is higher than $Z_{\max. \text{exp.}} =$ a few tens of micrometer, the GFA parameters that do not directly depend on T_g such as ΔT^* and ε show greater reliability to evaluate GFA for Mo-Ni-Si-B metallic glass with no clear T_g . The $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ metallic glass exhibits an exceptional thermal stability in metallic glass forming system ($T_x = 1112$ K), extremely high hardness (27.5 ± 2.2 GPa in Vickers hardness), and relatively low Young's modulus (364.3 ± 6.6 GPa). Furthermore, we carefully fabricate thin film metallic glass ($t \sim 100$ nm) using the $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ master alloy, which exhibits mechanical properties similar to fully amorphous $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ ribbon sample. Indeed, Mo-Ni-Si-B metallic glass exhibits much higher H/E ratio (0.075) and $H^2/(2E)$ value (1.05), far above the values of other metallic glasses and hard ceramic materials, such as VC, W_2B_5 , SiC, and TiN. These results suggest excellent wear resistance and high capability for elastic energy absorption (resilience) in Mo-Ni-Si-B metallic glass.

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References

- [1] A. Inoue, Stabilization of metallic supercooled liquid and bulk amorphous alloys, *Acta Mater.* **48** (2000) 279-306.
- [2] W.L. Johnson WL, Bulk glass-forming metallic alloys: science and technology, *MRS Bull.* **24** (1999) 42-56.
- [3] A.L. Greer, Metallic glasses... on the threshold, *Mater. Today*, **12** (2009) 14-22.
- [4] A. Peker, W.L. Johnson, A highly processable metallic glass: $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$, *Appl. Phys. Lett.* **63** (1993) 2342.
- [5] Y.C. Kim, W.T. Kim, D.H. Kim, A development of Ti-based bulk metallic glasses, *Mater. Sci. Eng. A* **375-377** (2004) 127-135.
- [6] D.H. Xu, B. Lohwongwatana, G. Duan, W.L. Johnson, C. Garland, Bulk metallic glass formation in binary Cu-rich alloy series- $\text{Cu}_{100-x}\text{Zr}_x$ ($x=34, 36, 38.2, 40$ at.%) and mechanical properties of bulk $\text{Cu}_{64}\text{Zr}_{36}$ glass, *Acta Mater.* **52** (2004) 2621-2624.
- [7] H.J. Chang, E.S. Park, Y.S. Jung, M.K. Kim, D.H. Kim, The effect of Zr addition in glass forming ability of Ni-Nb alloy system, *J. Alloys Compd.* **434-435** (2007) 156-159.
- [8] A. Inoue, B. Shen, H. Koshiba, H. Kato, A.R. Yavari, Cobalt-based bulk glassy alloy with ultrahigh strength and soft magnetic properties, *Nat Mater.* **2** (2003) 661-663.
- [9] D.H. Kim, J.M. Park, D.H. Kim, W.T. Kim, Development of quaternary Fe-B-Y-Nb bulk glassy alloys with high glass-forming ability, *J. Mater. Res.* **22** (2007) 471-477.
- [10] E.S. Park, D.H. Kim, Design of bulk metallic glasses with high glass forming ability and enhancement of plasticity in metallic glass matrix composites: A review, *Met. Mater. Int.* **11** (2005) 19-27.
- [11] X.M. Huang, C.T. Chang, Z.Y. Chang, X.D. Wang, Q.P. Cao, B.L. Shen, A. Inoue, J.Z. Jiang, Formation of bulk metallic glasses in the Fe-M-Y-B (M=transition metal) system, *J. Alloys Compd.* **460** (2008) 708-713.
- [12] M. Ohtsuki, K. Nagata, R. Tamura, S. Takeuchi, Tungsten-based metallic glasses

with high crystallization temperature, high modulus and high hardness, Mater. Trans. **46** (2005) 48-53.

[13] M. Sherif El-Eskandarany, S. Ishihara, A. Inoue, Mechanism of solid-state reaction for fabrication of new glassy $V_{45}Zr_{22}Ni_{22}Cu_{11}$ alloy powders and subsequent consolidation, J. Mater. Res. **18** (2003) 2435-2445.

[14] M. Sherif El-Eskandarany, M. Matsushita, A. Inoue, Mechanically driven solid state amorphization reaction of ball-milled $Nb_{50}Zr_{10}Al_{10}Ni_{10}Cu_{20}$ powders and the effect of annealing, J. Non-Cryst. Solids **312-314** (2002) 622-627.

[15] M. Sherif El-Eskandarany, W. Zhang, A. Inoue, Mechanically induced crystalline-glassy phase transformations of mechanically alloyed $Ta_{55}Zr_{10}Al_{10}Ni_{10}Cu_{15}$ multicomponent alloy powders, J. Alloys Compd. **350** (2003) 222-231.

[16] X.Q. Zhang, E. Ma, J. Xu, Mechanically alloyed multi-component Mo-based amorphous alloys with wide supercooled liquid region, J. Non-Cryst. Solids **352** (2006) 3985-3994.

[17] A. Leyland, A. Matthews, Review: plasma electrolysis for surface engineering, Wear **246** (2000) 1-11.

[18] M. Dao, L. Lu, R. Asaro, J. Dehossan, E. Ma, Toward a quantitative understanding of mechanical behavior of nanocrystalline metals, Acta Mater. **55** (2007) 4041-4065.

[19] D.B. Miracle, A structural model for metallic glasses, Nat. Mater. **3** (2004) 697-702.

[20] T.L. Oberle, Properties influencing wear of metals, J. Met. **3** (1951) 438G-439G.

[21] J.T. Burwell Jr, Survey of possible wear mechanisms, Wear **1** (1957) 119-141.

[22] C. Gammer, C. Mangler, C. Rentenberger, H.P. Karnthaler, Quantitative local profile analysis of nanomaterials by electron diffraction, Scripta Mater. **63** (2010) 312-315.

[23] S.A. Firstov, T.G. Rogul, S.N. Dub, V.L. Svetchnikov, H.W. Zandbergen, Structure,

mechanical behavior and nanohardness of chromium and molybdenum produced by magnetron sputtering. In: O.N. Senkov, D.B. Miracle, S.A. Firstov, editors. *Metallic materials with high structural efficiency*, Springer Netherlands **146** (2004) 341-346.

[24] E.O. Hall, The deformation and ageing of mild steel: III discussion of results, *Proc. Phys. Soc. B* **64** (1951) 747-753.

[25] N.J. Petch, The cleavage strength of polycrystals, *J. Iron Steel Inst.* **174** (1953) 25-28.

[26] E.O. Hall, Variation of hardness of metals with grain size, *Nature* **173** (1954) 948-949.

[27] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *J. Mater. Res.* **7** (1992) 1564-1583.

[28] G. Simmons, Single crystal elastic constants and calculated aggregate properties: a handbook. In: Wang H, editor. Cambridge, Mass., M.I.T. Press (1971).

[29] J. Menčík, D. Munz, E. Quandt, E.R. Weppelmann, M.V. Swain, Determination of elastic modulus of thin layers using nanoindentation, *J. Mater. Res.* **12** (1997) 2475-2484.

[30] G.M. Pharr, W.C. Oliver, Measurement of thin film mechanical properties using nanoindentation, *MRS Bull.* **17** (1992) 28-33.

[31] B. Jönsson, S. Hogmark, Hardness measurements of thin films, *Thin Solid Films* **114** (1984) 257-269.

[32] K. Rahmoun, A. Iost, V. Keryvin, G. Guillemot, N.E. Chabane Sari, A multilayer model for describing hardness variations of aged porous silicon low-dielectric-constant thin films, *Thin Solid Films* **518** (2009) 213-221.

[33] M.F. Doerner, W.D. Nix, A method for interpreting the data from depth-sensing indentation instruments, *J. Mater. Res.* **1** (1986) 601-609.

[34] R.B. King, Elastic analysis of some punch problems for a layered

medium, Int. J. Solids Struct. **23** (1987) 1657–1664.

[35] P. Nash, Phase diagrams of binary nickel alloys: ASM International (1991) 394.

[36] A. Takeuchi, A. Inoue, Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element, Mater. Trans. **46** (2005) 2817-2829.

[37] A.B. Gokhale, G.J. Abbaschian, The Mo-Si (Molybdenum-Silicon) system, J. Phase Equil. **12** (1991) 493-498.

[38] A. Takeuchi, A. Inoue, Calculations of mixing enthalpy and mismatch entropy for ternary amorphous alloys, Mater. Trans. **41** (2000) 1372-1378.

[39] D.B. Miracle, W.S. Sanders, O.N. Senkov, The influence of efficient atomic packing on the constitution of metallic glasses, Phil. Mag. **83** (2003) 2409-2428.

[40] T. Egami, Y. Waseda, Atomic size effect on the formability of metallic glasses, J. Non-Cryst Solids **64** (1984) 113-134.

[41] M. Naka, T. Masumoto, H.S. Chen, J. Physique **41** (1980) C8-839.

[42] C. Suryanarayana, A. Inoue, Iron-based bulk metallic glass, Int. Mater. Rev. **58** (2013) 131-166.

[43] J.M. Cadogan, S.J. Campbell, J. Jing, C.P. Foley, P. Kater, Y.W. Mai, Annealing embrittlement of Fe₇₈Si₉B₁₃(METGLAS-2605S2), Hyperfine Interactions, **226** (2014) 7-14.

[44] R. Roy, A.K. Majumdar, Thermomagnetic and transport properties of Metglass 2605SC and 2605, J. Magn. Magn. Mater. **25** (1981) 83-89.

[45] M.I. Baskes, Application of the embedded-atom method to covalent materials: a semiempirical potential for silicon, Phys. Rev. Lett. **59** (1987) 2666.

[46] Z.P. Lu, H. Tan, S.C. Ng, Y. Li, The correlation between reduced glass transition temperature and glass forming ability of bulk metallic glasses, Scripta Mater. **42** (2000) 667-673.

- [47] I.W. Donald, H.A. Davies, Prediction of glass-forming ability for metallic systems, *J. Non-Cryst. Solids* **30** (1978) 77-85.
- [48] D. Turnbull, Under what conditions can glass be formed?, *Contemp. Phys.* **10** (1969) 473-488.
- [49] A. Hrubý, Evaluation of glass-forming tendency by means of DTA, *Czech. J. Phys.* **22** (1972) 1187-1193.
- [50] Z.P. Lu, C.T. Liu, A new glass-forming ability criterion for bulk metallic glasses, *Acta Mater.* **50** (2002) 3501-3512.
- [51] E.S. Park, C.W. Ryu, W.T. Kim, D.H. Kim, A novel parameter to describe the glass-forming ability of alloys, *J. Appl. Phys.* **118** (2015) 064902.
- [52] J.-H. Kim, J.S. Park, H.K. Lim, W.T. Kim, D.H. Kim, Heating and cooling rate dependence of the parameters representing the glass forming ability in bulk metallic glasses, *J. Non-Cryst. Solids* **35** (2005) 1433-1440.
- [53] K. Mondal, B.S. Murty, On the parameters to assess the glass forming ability of liquids, *J. Non-Cryst. Solids* **351** (2005) 1366-1371.
- [54] H. Holleck, Material selection for hard coatings, *J. Vac. Sci. Technol. A* **4** (1986) 2661.
- [55] W.H. Wang, Elastic moduli and behaviors of metallic glasses, *J. Non-Cryst. Solids* **351** (2005) 1481-1485.
- [56] A. Öztürk, K.V. Ezirmik, K. Kazmanlı, M. Ürgen, O.L. Eryılmaz, A. Erdemir, Comparative tribological behaviors of TiN-, CrN- and MoN-Cu nanocomposite coatings, *Tribol. Int.* **41** (2008) 49-59.
- [57] D.R. Glasson, S.A.A. Jayaweera, Formation and reactivity of nitrides I. Review and introduction, *J. Appl. Chem.* **18** (1968) 65-77.

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Figure 1. XRD patterns of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($x = 0, 2, 5, 7, 10$) as-spun samples.

Figure 2. DSC thermograms of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($x = 5, 7, 10$) as-spun samples.

Figure 3. (a-e) SADPs with the inset patterns of azimuthally integrated intensity profiles and (f-j) BF-TEM images of as-spun $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ samples.

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Figure 5. Nanohardnesses and reduced elastic moduli of as-spun $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ samples depending on boron contents. (inset) Grain size variation of as-spun $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ samples depending on boron contents, with a red exponential fitting line.

Figure 6. (GI-)XRD patterns of the non-coated substrate and the coated substrate using $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloy.

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Figure 8. Heat of mixing relations (kJ/mol) [36] and atomic radius (Å) [40] of alloying elements in Mo-Ni-Si(-B) alloy system.

Figure 9. Comparison of relative atomic size ratios ($R_\alpha = r_{\text{solute}}/r_{\text{solvent}}$) and compositions for $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{100-x}\text{B}_x$ ($x = 0, 2, 5, 7, 10$) and selected Fe-metalloid metallic glasses with prediction as <10-8> γ vacant structure by dense cluster-packing model.

Figure 10. Classification of glass-forming alloy systems depending on the alloy components (modified from reference [1]).

Figure 11. (a) H/E and (b) $H^2/(2E)$ values of various glass-forming alloy systems depending on T_x .

Tables

Table 1. Nanohardness values of the coated & non-coated SUS substrate and as-spun ribbon of $(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ alloy

$(\text{Mo}_{45}\text{Ni}_{45}\text{Si}_{10})_{90}\text{B}_{10}$ (Amorphous)	H (GPa)
SUS substrate (H_s)	4.16 ± 0.46
Thin film + SUS (H_c)	7.50 ± 0.91
Thin film* (H_f)	28.7 ± 3.77
as-spun ribbon	24.6 ± 0.43

* Calculated from Jönsson & Hogmark model [31]

Table 2. Characteristic transformation temperatures (T_g , T_x , and T_l) and preparation method of the selected metallic glasses with high T_x

Alloy composition	T_g	T_x	T_l	Preparation Method	Ref.
$V_{45}Zr_{22}Ni_{22}Cu_{11}$	741	884	-	MA	[13]
$Ni_{60}Nb_{30}Zr_{10}$	875	902	1413	MC	[7]
$Fe_{68}Mo_4Y_6B_{22}$	915	944	1488	MS	[11]
$Nb_{50}Zr_{10}Al_{10}Ni_{10}Cu_{20}$	963	963	-	MA	[14]
$Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$	910	982	-	MC	[8]
$Ta_{55}Zr_{10}Ni_{10}Al_{10}Cu_{15}$	834	1004	-	MA	[15]
$(Mo_{45}Ni_{45}Si_{10})_{90}B_{10}$	1112	1112	1750	MS	This work
$W_{46}Ru_{37}B_{17}$	1149	1173	-	MS	[12]
$Mo_{44}Si_{26}Ta_5Zr_5Fe_3Co_{12}Y_5$	1202	1324	-	MA	[16]

** MA: Mechanical alloying/ MS: Melt-spinning / MC : Copper mold casting in millimeter scale

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

I	Co-Fe-(Nb, Zr, Ta)-B
	Fe-Co-Ln-(B, C)
	Fe-(Zr, Ln)-B
	Mo-Ni-Si-B
	Fe-Ni-(Si, P)-(B, C)
II	(Al, Ga)-Fe-metalloid
III	Ce-Al-Cu-(Fe, Nb, Co)
	Cu-(Zr, Hf)-Al
	(Zr, Ln)-Al-(Co, Ni, Cu)
	Ti-Ni-Cu-Sn
	Ti-Zr-Cu-Pd-Sn
	Zr-Ti-Ni-Cu-Be
	Mg-(Cu, Ni)-Ln
IV	Au-(Ag, Pd)-Cu-Si
	(Pd, Pt)-(Cu, Ni)-(Si, P)
	(Au, Pd)-Si
V	Cu-Zr
	Ni-Nb

Figure 10

Figure 11