A Mo₄₄Si₂₆Ta₁₁Zr₅Fe₃Co₁₂Y₅ multi-component amorphous alloy was developed via mechanically alloying (MA). It exhibits a record high glass transition temperature of 1202 K and crystallization temperature of 1324 K, an ultrahigh hardness of 18 GPa, as well as a wide supercooled liquid region (122 K) promising for processing through powder metallurgy routes. Here we present the details of the phase evolution during MA and discuss the effects of alloying elements, starting from the Mo–Co and Mo–Si binary systems, through two series of ternary alloys, eventually reaching the desired properties by selecting additional components. The propensity for glass formation and the high thermal stability were interpreted in terms of the negative heat of mixing of the elements introduced, as well as a uniform coverage spanning a wide range of atomic sizes.

1. Introduction

As a novel class of engineering materials, metallic glasses due to exceptional mechanical properties, such as high strength and high elastic strain limit, have been extensively investigated [1–4]. More recently, a large number of new alloys with exceptional glass-forming ability (GFA), allowing the formation of bulk metallic glasses (BMGs) using conventional casting, have been discovered. However, they have limited thermal stability against crystallization, which restricts the service temperature for these thermodynamically-metastable glassy alloys. The thermal stability of the glassy alloy is usually characterized by the glass transition temperature \( T_g \) or onset temperature of crystallization \( T_x \). Meanwhile, the \( T_g \) of glass-forming alloys approximately scales with the melting temperature of the main element in the alloy. Usually, increasing the \( T_g \) of the alloy is also directly accompanied by an increase of the strength of the metallic glasses [1]. A direct correlation between yield strength \( \sigma_y \) (or \( H_v/3 \), where \( H_v \) is the Vickers hardness) and \( T_g \) is demonstrated with a linear fit. Also, such a plot shows a good linear trend, in approximate agreement with the \( \sigma_y = 55\Delta T_g/V \) relation recently described by Yang et al. [5], where \( \Delta T_g = T_g - T_0 \), and \( T_0 \) and \( V \) is room temperature and the mol volume, respectively. Therefore, amorphous alloys with high \( T_g \) are desirable as they promise to exhibit both high thermal stability and high strength.

In this regard, amorphous alloys based on refractory metals, such as W, Mo, Ta or Nb, are obviously of interest as promising candidates to achieve ultrahigh strength and thermal stability. Unfortunately, the high melting temperature of refractory metals and the absence of eutectic
reactions at low temperatures make it difficult to fabricate glassy alloys in refractory systems through melt casting. While glassy foils or ribbons have been prepared through melt undercooling in Nb–Ni and Ta–Ni [6], W–Ru-based or Mo–Ru-based [7–11] and Mo–Si–B [12] alloys, BMGs have not been achieved based on these refractory metals so far. In the present work, therefore, we adopt the mechanical alloying (MA) route to vitrify the alloy powder blends of refractory metals at room temperature. We will develop an understanding as to how the phase evolution induced by glassification under high energy ball milling was studied in several Mo–M (M = Ni, Fe, Co, Si) binary systems at equiatomic composition (Mo50M50), to select a base alloy. Then, by taking into account atomic size distribution and the heat of mixing between the components, Mo–Co–Si ternary alloys and higher-order Mo-based alloys were designed and synthesized via MA to eventually form a glassy phase with unprecedented high thermal stability, wide supercooled liquid region and ultrahigh hardness.  

2. Experimental

The starting materials for MA were commercially available Mo, Co, Si, Fe, Zr and Ta powders with 99.5% or higher purity. The powder particle size is smaller than 75 μm. Co–Y ingots as an intermediate alloy were prepared by arc melting the Co and Y pieces with purity higher than 99.9% under a Ti-gettered argon atmosphere in a water-cooled copper crucible, and then crushed into fragments smaller than 500 μm in size. The elemental powders (or with prealloyed Co–Y fragments) were blended to give the designed compositions. MA was performed in a SPEX8000 mill cooled by flowing air. The ball-to-powder weight ratio was fixed at 5:1. To avoid the cold welding of the powders on the walls of the milling vial, stearic acid (C18H36O2) (about 0.5 wt.%)) was added as a process control agent (PCA). Together with hardened steel balls, the powder mixture of the designed composition was loaded in a hardened steel vial under an argon-filled glove box with less than 1 ppm O2 and H2O.

The as-milled powders were analyzed using X-ray diffraction (XRD) in a Rigaku D/max 2400 diffractometer with monochromated Cu Kα radiation. The iron contents of the milled samples varied between 1 and 3 at.% depending on the Mo content, as determined using inductively coupled plasma emission spectroscopy (ICP10P, ARL). The oxygen contents of the samples were determined to be below 0.22 wt.% using a LECO TC-436 system.

The glass transition and crystallization behavior of the as-milled samples were investigated using a Netzsch differential scanning calorimeter (DSC 404 C Pegasus) with an alumina container at a heating rate of 20 K/min under flowing purified argon after being evacuated to a vacuum of \(\sim 10^{-3}\) Torr. A second run under identical conditions was conducted to determine the baseline. To determine the onset temperature of glass transition, \(T_g\), the sample was heated to a temperature below \(T_x\) to reach a relaxed state for resolving the initial change in the baseline. To confirm the reproducibility of the results, at least three DSC samples of each alloy were measured.

The morphology of the cross-section for representative ball-milled powders was observed in a Cambridge S360 scanning electron microscope (SEM). For transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) observations, the samples were prepared by first embedding the powder particles in a copper foil via electrodeposition for mechanically thinning and subsequently ion milling to electron transparency. The TEM/HRTEM observations were carried out in a Tecnai G2 F30 transmission electron microscope.

To get the strength information for the alloy, nanoindentation measurements were performed on the cross-sections of the as-milled Mo44Si26Ta5Zr5Fe2Co12Y5 particles using an instrumented Hysitron TriboIndenter with a Berkovich indenter tip. The indentation size is approximately 1 μm in the middle section of the particles with size of 20–40 μm which are much larger compared with the indentation. The sample was prepared by mixing the as-milled particles with a molten Mg–Cu–Y BMG former and the melt was chill-cast into a 4-mm diameter rod [25]. This procedure of embedding the particles into a matrix alloy that is also a hard glass minimizes the matrix effect during nanoindentation testing. The melting point of the selected glass former is far below the \(T_g\) of the Mo-based glassy alloy such that crystallization during the solidification process and interdiffusion reaction between the matrix and the particles are both prevented. The chill-cast ‘composite’ rod was ground using SiC grinding papers and then polished with diamond paste. Specially designed jig was employed during the nanoindentation sample preparation to ensure
the parallelism of the rod samples’ top (tested) and bottom surface. For all the measurements, when the load was larger than 2 mN, the hardness data did not show significant variation, so the load was set as 2, 5 and 10 mN. For every load, at least 10 indentations were made on powder particles of different diameters of about 20–40 µm and the average value were reported.

3. Results

3.1. Milling-induced amorphization in Mo50M50 binary alloys

Fig. 1 shows the XRD patterns of powder blends with the nominal composition of Mo50M50 (M = Ni, Fe, Co and Si) subjected to milling of 32 h. For the alloys of M = Ni, Fe and Co, the diffraction peaks of Mo superimpose on the diffuse maxima of an amorphous phase, indicating that the milled products are a mixture of amorphous phase and Mo-rich solid solution (S.S.). In all cases, full amorphization was not achieved, and the amorphous phase formed was M-rich rather than Mo-rich. In contrast, the formation of amorphous phase was obviously more favorable in the Mo–Si case, although some MoSi2 and Mo crystals remained detectable in the XRD patterns. The line profiles at 2θ = 30–55° of the XRD patterns for the milled Mo–Ni(Fe, Co) alloys as shown in Fig. 1, are fitted using an Origin peak-fitting program with the Pearson VII function. The integrated intensity of the Mo(110) diffraction peaks and the diffuse maximum of amorphous phase are determined. Based on the integrated intensity, the volume fraction of the amorphous phase ($V_f$) of Mo50M50 (M = Ni, Fe and Co) is semi-quantitatively estimated to be about 70%, 70% and 80%, respectively. The composition of the amorphous phase formed in the ball-milled Mo50M50 alloys (M = Ni, Fe and Co) was estimated to be about Mo50Ni70, Mo50Fe70, Mo38Co62, respectively, using a method described in Ref. [20]:

$$\frac{x}{y} = \frac{(1-R)}{(1+R)}$$

where $x$ and $y$ are the atomic fractions of the two components in alloy $XY$ and $R$ is the ratio of the relative area of diffuse halo from the amorphous phase to that of the main Bragg diffraction peak of the residual crystalline phase.

In conclusion, milling-induced amorphization occurs more readily in the Mo–Co and Mo–Si alloys among the investigated binary systems. This is one of the reasons why the Mo–Co–Si ternary alloys are selected in the following to examine the feasibility to fully amorphize via MA route.

3.2. Mechanically milled Mo–Co–Si ternary alloys

3.2.1. The Mo50Co50–xSi$_x$ ($x = 10, 30, 35$) series

Substituting the Co with Si in the Mo50Co50 alloy led to a series of alloys, Mo50Co50–xSi$_x$ ($x = 10, 30, 35$). Fig. 2 illustrates the XRD patterns of these alloys milled for 32 h. Compared with the Mo–Co and Mo–Si binary alloys ($x = 0$ and 50), the diffraction intensity of the unreacted crystalline Mo was gradually weakened with increasing Si content. At $x = 35$ (Mo50Si35Co15), the diffraction halo from amorphous phase is predominant, and only a small
fraction of crystalline phase remains visible. Based on fitting the XRD line profiles, the variation of the amorphous volume fraction with the Si content was estimated, as shown in Fig. 2 as an inset. The optimum composition for the amorphization is located at 35% Si.

To reveal the structural evolution during milling, the powder blend with a nominal composition of Mo_{50}Si_{35}Co_{15} was milled for different times up to 48 h. Fig. 3(a) shows XRD patterns of the milled alloys. After milling for 16 h, the diffraction peaks of Si and Co crystals disappeared completely. However, the diffraction peaks of Mo crystals, obviously broadened due to grain refinement and internal strain, were found superimposed on the diffuse peak of amorphous phase. On further milling to 24 h, the diffraction intensity from crystalline Mo was reduced, accompanied by more amorphization. At 32 h, the Bragg peaks corresponding to Mo were no longer detectable. The full width at half maximum (FWHM) of the diffuse peak of the amorphous phase increased further after milling for 48 h, and the peak became more symmetric. Further extending the milling time to 60 h, the XRD patterns did not change obviously compared with that of 48 h. In other words, the system has reached a steady state after 48 h of MA. On the other hand, extending the milling time could bring excess contamination and increase the time cost. Therefore, we prefer to resort to multi-component alloying rather than prolonging milling time to achieve a fully amorphous alloy. For all the samples discussed in the rest of this paper, the milling time was fixed at 48 h. In other words, the system has reached a steady state after 48 h of MA. On the other hand, extending the milling time could bring excess contamination and increase the time cost. We therefore prefer to resort to multi-component alloying rather than prolonging milling time to achieve a fully amorphous alloy. For all the samples discussed in the rest of this paper, the milling time was fixed at 48 h. This milling time is chosen to assure that the milling has proceeded sufficiently long for the samples to reach a steady state, but short enough to avoid excessive contamination from the milling media. A fixed milling duration makes it convenient to compare the effects when more and more components are introduced into the alloy.

Fig. 3(b) shows DSC scans of Mo_{50}Si_{35}Co_{15} alloy milled for different times. For the sample of milling to 16 h, the heat release caused by crystallization was detected, indicating the formation of amorphous phase. Extending the milling time lead to an increase of heat of crystallization, which associated with the increase of fraction of amorphous phase. Up to 32 h, the milling-induced amorphization approached to a steady state, indicated by a fact that the crystallization temperature and heat of crystallization is no longer changed obviously to be 1164 K and 3.58 kJ/mol for 32 h and 1164 K and 3.65 kJ/mol for 48 h, respectively. Nevertheless, no significant signal due to the glass transition appears in the scan for the final product. On further improving the thermal stability of the amorphous phase, it is necessary to increase the Mo content in the alloy. Then, based on the Mo_{50}Si_{35}Co_{15} alloy, here the Si:Co ratio was fixed at 7:3, amorphization in a series of alloys, Mo_{y}(Si_{0.7}Co_{0.3})_{100-y} under ball milling were investigated subsequently.

3.2.2. The Mo_{y}(Si_{0.7}Co_{0.3})_{100-y} series

For the ball-milled Mo_{y}(Si_{0.7}Co_{0.3})_{100-y} ternary alloys, predominant amorphous phase was obtained when y = 45, 50 and 55, indicated by XRD patterns as shown in Fig. 4(a). When the Mo content at 60% and 70% (y = 60 and 70), the products were a mixture of amorphous phase and Mo S.S. Meanwhile, it was found from the DSC results shown in Fig. 4(b) that the $T_x$ increased with the increase of y and reached the maximum of 1244 K when y = 60. In contrast, the $T_x$ goes down to 1171 K when y = 70. We note that the $T_x$ of Mo_{60}Si_{28}Co_{12} alloy is elevated by 96 K compared with the Mo_{50}Si_{35}Co_{15} alloy, but it still does not show a glass-transition signal in the corresponding DSC scan (see Fig. 4(b), y = 60).

To obtain bulk Mo-based amorphous alloy, the presence of a wide supercooled liquid region is a must, because the amorphous alloy powders are processable only in that temperature span. For attaining a fully amorphous alloy with high crystallization temperature and a supercooled liquid region, the Mo_{60}Si_{28}Co_{12} alloy was selected as a...
new starting point and more alloying elements were introduced into the system, as described below.

3.3. Structure and thermal stability changes with additional alloying

Fig. 5(a) illustrates the XRD patterns of the multi-component Mo-based alloy powders after 48 h of MA. For the Mo60Si28Co12 alloy milled for 48 h, all the diffraction peaks of Co and Si disappeared and only the diffraction peaks of Mo were superimposed on the diffuse diffraction maximum of the amorphous phase. When 5% Mo was substituted by Y (with a larger atomic radius of 0.180 nm) to form a quaternary alloy, the diffraction peaks of Mo became less pronounced. Additional substitution of Mo with 10% Ta led to the quinary Mo45Si28Ta10Co12Y5 composition. More amorphous phase was obtained and all the diffraction peaks of Mo almost disappeared except for the Mo(110) peak. Adjusting the composition further to Mo44Si26Ta5Zr5Fe3Co12Y5, only the typical diffuse peaks of an amorphous phase can be observed at 2θ = 30–50°. This indicates that the ball-milled Mo44Si26Ta5Zr5Fe3Co12Y5 alloy is a fully amorphous alloy within XRD resolution. The volume fraction of the amorphous phase estimated on the line profiles fitting is 88% for Mo60Si28Co12, 91% for Mo55Si28Co12Y5, 98% for Mo45Si28Ta10Co12Y5 and 100% for Mo44Si26Ta5Zr5Fe3Co12Y5, respectively. The FWHM of the amorphous halo was broadened from 6.48° for Mo60Si28Co12 ternary alloy to 7.55° for Mo44Si26Ta5Zr5Fe3Co12Y5 high-order alloy. The volume fraction of amorphous phase and FWHM increased step by step when the selected elements were gradually introduced into the Mo60Si28Co12 alloy. It indicates that the multi-component alloying enhanced the MA-induced glass formation.

The DSC scans of the as-milled alloys are compared in Fig. 5(b). The data for Tg, Tx, ΔTx and the enthalpy of crystallization (ΔHf) obtained from the DSC measurements, are listed in Table 1 for all the alloys. The
corresponding data of other refractory-metal-based glassy alloys [11,18,19,26] are included for comparison. The general trend from Fig. 5(b) is that as the partially amorphous ternary Mo$_{60}$Si$_{28}$Co$_{12}$ alloy evolves into the multi-component, near-fully amorphous Mo$_{44}$Si$_{26}$Ta$_{5}$Zr$_{5}$-Fe$_{3}$Co$_{12}$Y$_{5}$ by introducing additional alloying elements, the alloy’s thermal stability is enhanced remarkably. The primary manifests of thermal stability enhancement are the emergence of the glass transition signal and the supercooled liquid region. The $T_x$ is increased by 72 K from the 1252 K of Mo$_{60}$Si$_{28}$Co$_{12}$ to the 1324 K of Mo$_{44}$Si$_{26}$Ta$_{5}$Zr$_{5}$-Fe$_{3}$Co$_{12}$Y$_{5}$. While the ternary Mo$_{60}$Si$_{28}$Co$_{12}$ alloy showed no endothermic signal corresponding to glass transition, the Mo$_{55}$Si$_{28}$Co$_{12}$Y$_{5}$ alloy begins to exhibit a well-defined glass transition event. When 10% Mo is substituted by Ta, the $T_g$, $T_x$, $\Delta T_x$ all increased further. For the Mo$_{44}$Si$_{26}$-Ta$_{5}$Zr$_{3}$Fe$_{3}$Co$_{12}$Y$_{5}$ alloy, the $T_g$, $T_x$ are as high as 1202 ± 3 K and 1324 ± 3 K, respectively, and the $\Delta T_x$ is as large as 122 ± 3 K. It is noteworthy that the $T_g$ and $T_x$ of Mo$_{44}$Si$_{26}$Ta$_{5}$Zr$_{3}$Fe$_{3}$Co$_{12}$Y$_{5}$ glassy alloy are only lower than that of Ta$_{55}$Ir$_{45}$ and W$_{56}$Ta$_{24}$Si$_{10}$B$_{10}$ amorphous alloys [27], indicating extraordinary thermal stability of the glass. In addition, the bell-shaped isothermal DSC traces shown in Fig. 6 demonstrate the crystallization as a nucleation and growth process [28], which further verifies the as-milled Mo$_{44}$Si$_{26}$Ta$_{5}$Zr$_{3}$Fe$_{3}$Co$_{12}$Y$_{5}$ powders are predominantly amorphous. Fig. 7(a) and (b) shows the SEM image taken in the backscattering mode of the morphology of the cross-section of the Mo$_{44}$Si$_{26}$Ta$_{5}$Zr$_{3}$Fe$_{3}$Co$_{12}$Y$_{5}$ powders after Table 1

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$\Delta H_x$ (kJ/mol)</th>
<th>Preparation methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$<em>{60}$Si$</em>{28}$Co$_{12}$</td>
<td>–</td>
<td>1252</td>
<td>–</td>
<td>3.47 ± 0.13</td>
<td>MA$^a$</td>
<td>This work</td>
</tr>
<tr>
<td>Mo$<em>{55}$Si$</em>{28}$Co$<em>{12}$Y$</em>{5}$</td>
<td>1136</td>
<td>1244</td>
<td>108</td>
<td>3.78 ± 0.16</td>
<td>MA$^a$</td>
<td>[11]</td>
</tr>
<tr>
<td>Mo$<em>{45}$Si$</em>{28}$Ta$<em>{10}$Co$</em>{12}$Y$_{5}$</td>
<td>1138</td>
<td>1263</td>
<td>125</td>
<td>3.95 ± 0.12</td>
<td>MA$^a$</td>
<td>[18]</td>
</tr>
<tr>
<td>Mo$<em>{44}$Si$</em>{26}$Ta$<em>{5}$Zr$</em>{5}$Fe$<em>{3}$Co$</em>{12}$Y$_{5}$</td>
<td>1202</td>
<td>1324</td>
<td>122</td>
<td>4.13 ± 0.08</td>
<td>MA$^a$</td>
<td>[19]</td>
</tr>
</tbody>
</table>

Corresponding data of other refractory metal based glassy alloys are included for comparison.

$^a$ Mechanical alloying.

$^b$ Melt spinning.

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Fig. 6. Isothermal DSC curves at several temperatures of ball milled Mo$_{44}$Si$_{26}$Ta$_{5}$Zr$_{3}$Fe$_{3}$Co$_{12}$Y$_{5}$ amorphous alloy.

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Fig. 7. SEM images in backscattering mode of the cross-section of the Mo$_{44}$Si$_{26}$Ta$_{5}$Zr$_{3}$Fe$_{3}$Co$_{12}$Y$_{5}$ alloy powder ball milled for (a) 8 and (b) 48 h.
8 and 48 h MA, respectively. For the 8 h powders, the microstructure has the appearance of a ‘sandwich’ composite, composed of alternating white layer and gray layer. It is revealed by EDX analysis that the white layer is richer in Mo and the gray layer is Mo diluted. A similar structure has been found in early ball milling stages of other alloy systems (especially for binary systems) [29,30]. When the MA time was extended to 48 h, the average powder particle size was reduced to about 20 μm, from the 80 μm of the 8-h samples. The uniform and contrast-less morphology suggests nearly a single fully amorphous phase.

The TEM bright field image and the corresponding selected area electron diffraction (SAED) patterns of the 48 h-milled Mo44Si26Ta5Zr5Fe3Co12Y5 powders are displayed in Fig. 8. The SAED pattern for the typical featureless areas (Fig. 8(a)) shows a broad halo, as seen in Fig. 8(b). It indicates that the amorphous phase is dominant in this sample. TEM observations also revealed that there were residual crystalline particles with sizes of about 5–20 nm embedded in the contrast-less amorphous ‘matrix’ and the crystalline fraction is very small. The XRD Bragg diffractions from these small particles are so weak and extensively broadened that one cannot tell them apart from the background of the amorphous phase (Fig. 5(a)). The SAED (Fig. 8(c)) and EDS results reveal that the crystalline particles are Mo(Si, Co, Ta) S.S. The structural features of the amorphous area and the embedded crystalline particles are also examined using high-resolution TEM imaging, as seen in Fig. 9(a) and (b). The fringe spacing for the crystals was determined to be 2.22 ± 0.02 Å, which is consistent with the d-space of the {101} plane of the bcc Mo phase (2.225 Å). Apparently, although there are no visible XRD Bragg peaks for the Mo44Si26Ta5Zr5Fe3Co12Y5 powders after 48 h MA, there are still some residual nanostructured Mo S.S. crystals.

3.4. Nanoindentation measurements

The Young’s modulus and hardness of as-milled Mo44Si26Ta5Zr5Fe3Co12Y5 powders were determined using nanoindentation loading–unloading curves. Fig. 10 displays a typical loading–unloading curve in a case of 5 mN load. The inset of Fig. 10 is the morphology of the corresponding indentation. The apparent Young’s modulus is obtained from the unloading curves by measuring the pressing force (P) vs displacement depth (h) relation continuously through repeated loading and unloading. The material’s Young’s modulus was obtained through Eq. (1) [31] to remove the indenter’s effect:

\[
\frac{1}{E_i} = \frac{(1 - \nu_s^2)}{E_s} + \frac{(1 - \nu_i^2)}{E_i}
\]

where \(E_r\) is the reduced Young’s modulus, \(\nu\) is Poisson’s ratio and subscripts \(s\) and \(i\) signify specimen and indenter,
pipe diffusion plays a decisive role for intermixing the ele-
order alloy system such as Zr–Al–Ni–Cu, that dislocation
Furthermore, it was proposed recently, even for the high-
polymorphous transition to the amorphous state[34,35].
urated Zr solid solution becomes unstable and undergoes a
is of interest to note in the binary Zr–Al system that when
the Al content exceeds a critical concentration the supersat-
reactions are responsible for the amorphization [29,33]. It
is of interest to note in the binary Zr–Al system that when
the Al content exceeds a critical concentration the supersat-
urated Zr solid solution becomes unstable and undergoes a
diffusion plays a decisive role for intermixing the ele-
ments and promoting amorphization in the solid-state
reaction process [36].
On the other hand, atomic size effects on glass formation
of the alloys have been highly emphasized as a crucial issue.
Typically, Egami [37,38] developed a topological model for
amorphization of binary alloys. According to this model,
amorphization occurs when the local atomic strains gener-
ated by the size differences between the substitutional sol-
ute and the solvent elements reach a critical level, leading
to a topological instability of the crystalline lattice. Miracle
et al. [39,40] also established models based on atomic size
ratios and used the correlations observed to offer a structural
basis for the selection of candidate solute elements and
concentrations. Moreover, Guo et al. [41] suggests that
a uniform separation in the atomic size as well as a wider
atomic size distribution range would enhance the glass
formation.
Melt-quenching and MA are different kinetic pathways
to reach a thermodynamically metastable amorphous state.
In both cases, amorphization occurs below $T_g$, and because
the metallic glass can be considered as a highly under-
cooled liquid, an analogy between the crystalline-to-amor-
phous phase transformation and melting has been drawn
[42–44]. Arguments based on the models discussed above
may thus be borrowed to explain the amorphization via
MA. Senkov et al. [45] concluded that the larger is the atom
size of the solvent element; the easier is the amorphization.
To achieve global instability of the crystal lattice, the
atomic radius ratios of solute and solvent elements should
fall in a particular range. This range becomes wider when
the size of the solvent element increases. $T_g$ increases when
the atom size of the solvent element and concentration of
the solute increase.
The atomic radius and the normalized atomic radius
(i.e., atomic size ratio), $R_{\text{solute}} = R_i/R_{\text{Mo,}}$ of the elements
involved in this study and all the data of heat of mixing
[46] between Mo and the participating alloying elements
are listed in Table 2. We start our explanation by first
looking at the heat of mixing factor. Compared with that
of Ni–Nb, Ni–Zr and Zr–Al ($-30$, $-49$ and $-30$ kJ/mol,
respectively) binary systems that can be easily amorphized
via MA, the smaller magnitude of the negative heat of
mixing between Mo and Fe, Co and Ni leads to a smaller
driving force for amorphization. This may be a reason
why fully amorphous alloys can not be achieved in ball-
milled Mo$_{30}$Si$_{30}$ (M = Ni, Fe, Co) (see Fig. 1). As illustrated
in Fig. 4, when the third element Si was added, its large negative heat of mixing with Mo may have

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Si} & \textbf{Ta} & \textbf{Zr} & \textbf{Fe} & \textbf{Co} & \textbf{Y} \\
\hline
$R_i$ (nm) & 0.115 & 0.143 & 0.160 & 0.124 & 0.125 & 0.180 \\
$R_{\text{solute}} (R_i/R_{\text{Mo}})$ & 0.845 & 1.051 & 1.176 & 0.912 & 0.919 & 1.324 \\
$\Delta H_{\text{mix}}$ (kJ/mol) & $-20$ & $-7$ & $-12$ & $-1$ & $-4$ & $+11$ \\
\hline
\end{tabular}
\caption{Atomic radius and the atomic size ratio for elements involved in this study and the heat of mixing between Mo and these elements}
\end{table}
helped the alloying and amorphization: the amount of the residual Mo crystal was reduced gradually and the amorphous alloy was obtained when the Si content reached 55%.

To destabilize the Mo S.S., a strategy is by enlarging the atomic size mismatch with host element Mo and the atomic size distribution range. It is interesting to note that the addition of 5% Y, which has a larger atomic size ($R_\text{Y} = 0.180$ nm), results in higher amorphous fraction and enhanced the thermal stability of the supercooled liquid (see Fig. 5). The introduction of Y significantly extends the atomic size distribution range and the large size mismatch causes the destabilization of the Mo via atomic level stresses. Evidently, the composition of the eventual Mo$_{44}$Si$_{26}$Ta$_5$Zr$_5$Fe$_3$Co$_{12}$Y$_5$ alloy represents a uniform separation in the atomic size as well as a wider atomic size distribution range, a known recipe to enhance the metastability of the supercooled liquid by increasing the packing density of atoms [38–41,45]. The uniform atomic size distribution can produce larger atomic level strains that soften and collapse the crystal lattice [45]. Since the residual crystalline are always Mo S.S. in the milling cases (see Figs. 1,2,4(a) and 5(a)), inducing the elements having a larger atomic size difference with Mo seems to be an important issue to destabilize the Mo S.S. This effect appears to be present in our case, as the competing crystalline phase indeed faded away when the elements (Co, Y, Ta, Zr, Fe) were added (see Fig. 5).

The record high $T_g$ and $T_x$ of the Mo$_{44}$Si$_{26}$Ta$_5$Zr$_5$Fe$_3$Co$_{12}$Y$_5$ glassy alloy indicate its extraordinary thermal stability. Meanwhile, the width of the supercooled liquid region exceeds 120 K, which is comparable to the value of highly processable Zr-based metallic glasses (the largest $\Delta T_g$ = 135 K [47]). The extraordinary thermal stability can be partly attributed to the intrinsic properties [32] of the host metal Mo, i.e., its high elastic constant and high melting point. But elements W and Ta have even higher elastic constant and melting points than Mo, yet their alloys are not as stable (Table 1). Hence the extraordinary thermal stability of Mo$_{44}$Si$_{26}$Ta$_5$Zr$_5$Fe$_3$Co$_{12}$Y$_5$ should be partly attributed to the a uniform separation in the atomic size as well as a wider atomic size distribution range of this alloy, increasing the stability of the supercooled liquid state of the alloy to hinder the nucleation of crystalline phase.

The metalloid element Si may be another important factor responsible for the achievement of record high thermal stability. Si has very negative heat of mixing with the host element Mo and others constituents. Note that the Mo/Si ratio in the alloys shown in Fig. 2 is almost same as that in Mo$_5$Si$_3$. In its crystalline form, Mo$_5$Si$_3$ has the highest melting point (2453 K) among the silicides in the Mo–Si system and a high Young’s modulus of 323 GPa. Its high strength and stability even at elevated temperatures reflects the pronounced covalent components in its atomic bonding [48,49]. Such advantages are also reflected in Mo–Si based amorphous alloys.

5. Conclusions

(1) Under ball milling, full amorphization cannot be realized in the Mo$_{50}$M$_{50}$ (M = Ni, Fe, Co) binary alloys. The MA products are mixtures of M-rich amorphous phase and nanograin Mo (M) solid solution. Among them, Mo$_{50}$Co$_{50}$ exhibits the best tendency for amorphization (the amorphous volume fraction is up to about 80%). In the Mo$_{50}$Si$_{50}$ alloy, the residual crystalline phases are Mo(Si) S.S. together with the MoSi$_2$ compound.

(2) For the ternary alloys, the amorphous volume fraction increases with increasing Si content in the ball-milled Mo$_{50}$Co$_{50}$–xSi$_x$ (x = 10, 30, 35) series. At x = 35, the product was nearly a single amorphous phase, within XRD resolution. In the case of the Mo$_x$(Si$_{60}$Co$_{40}$)$_{100-x}$ series, the product was predominantly amorphous when 45 $\leq$ x $\leq$ 55, whereas a mixture of amorphous phase and Mo S.S. formed when x increased to 60 and 70. The crystallization temperature of amorphous phase is dependent on the Mo content. The maximum $T_x$ is 1244 K for the Mo$_{60}$(Si$_{50}$Co$_{50}$)$_{40}$ alloy.

(3) Based on the Mo$_{60}$Si$_{28}$Co$_{12}$ alloy, elements Y, Ta, Zr and Fe were added to enhance the amorphization and the thermal stability. These elements were chosen based on their negative heat of mixing with the host element, and the uniform coverage of atomic radii in an enlarged span of atomic sizes leading to large and varied atomic radius mismatch between the solvent and solute elements. We discovered a good glass former at Mo$_{44}$Si$_{26}$Ta$_5$Zr$_5$Fe$_3$Co$_{12}$Y$_5$, which exhibits a record high glass transition temperature ($T_g$) of 1202 K and crystallization temperature ($T_c$) of 1324 K, accompanied by a large supercooled liquid region ($\Delta T_c$) of 122 K. A small amount of Mo S.S. nanocrystals 5–20 nm in size existed in the final ball-milled products. Such a Mo-based glassy alloy also has an ultrahigh hardness of 18 GPa (strength estimated to be of the order of 6 GPa using $\sigma = 1/3H_c$) and Young’s modulus of 235 GPa.

The structural stability against crystallization may render such an alloy useful as a strong/hard load-bearing or surface-coating material at relatively high temperatures. Its large $\Delta T_c$ leads to the possibility of consolidation into bulk parts utilizing the viscous flow properties of the supercooled liquid.

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