Amorphization Tendency of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ during Mechanical Alloying

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Pure elemental powders of Ti, Zr, Cu and Ni corresponding to the compositions of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ (at%) were subjected to mechanical alloying on a low energy milling machine in the present work. The premixed powders of the above two compositions underwent the following transformations during mechanical alloying up to 100 h: μm -sized (Ti, Zr, Cu, Ni) $\rightarrow$ nm-sized (Ti, Zr, Cu, Ni) $\rightarrow$ amorphous + a small amount of nm-sized crystallites. The 100-h milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ sample was found to exhibit an excellent thermal stability against crystallization with the crystallization temperature of about 200 K higher than that of the as-quenched amorphous counterpart. Contrary to the previous rapid quenching result, amorphous phase is easier to occur in $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ than in $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ by MA, indicating that the glass forming ability by rapid quenching is different from that by MA.

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I. Introduction

The chemical compositions of conventional as-quenched metallic glasses usually lie in the vicinity of the deep eutectic points of phase diagrams. Recently, studies on the formation of bulk amorphous materials with wide supercooled liquid regions by using the traditional melt quenching technique are quite active in the field of materials science and engineering due to their much promise for technical applications. Attempts have been tried in several alloy systems and success has been found in Mg-Ln-TM⁽¹⁾⁽²⁾, Ln-Al-TM⁽³⁾⁽⁴⁾, Ti-Zr-TM⁽⁵⁾⁽⁶⁾, Zr-Al-TM⁽⁷⁾⁽⁸⁾ and Ti-Zr-Be-TM⁽⁹⁾⁽¹⁰⁾ (TM=transition metal) etc. Johnson *et al.*⁽⁶⁾ showed that the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy can be cast into amorphous ribbons 4 mm thick at least although its composition is off the quaternary eutectic point. However, the quaternary eutectic composition, $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$, can not be cast to an as thin as 0.5-mm thick amorphous ribbon.

Following the early research works by Benjamin⁽¹¹⁾⁽¹²⁾ on oxide-dispersion strengthened superalloys by mechanical alloying (MA), a large number of investigations have been focused on this unique technique to produce non-equilibrium structures such as amorphous, quasicrystal, nanocrystal and other metastable phases in the past two decades. Investigations on MA of the multicomponent easy glass forming the alloy systems mentioned above are of considerable interests because MA leads to amorphization *via* a solid-state reaction process. In milling, the elemental powders are repeatedly deformed, fractured and cold welded during the ball-powder-ball collisions. Due to highly energetic compressive impact force, the

metals join to create diffusion couples, *i.e.*, clean interfaces where interdiffusion of the associated atoms starts and eventually results in the formation of a homogeneous phase. A large number of early researches on MA of binary alloys such as Ni-Zr⁽¹³⁾, Ti-Ni⁽¹⁴⁾, Ti-Cu⁽¹⁵⁾ and ternary alloys such as Ti-Ni-Cu⁽¹⁶⁾⁽¹⁷⁾ clearly revealed amorphization in these alloy systems. Thus, as an alternative technique MA may be an effective way to prepare multicomponent amorphous alloys in a wide composition range. Up to now the pre-existing theory⁽¹⁴⁾ on amorphization induced by MA has been mainly based on the experiments of binary alloy systems. Thus, MA of a multicomponent system and its comparison with the rapid quenching result may provide us useful information about the amorphization mechanism of multicomponent system during MA. So far little work, however, has been done in this field. In the present work, we report on MA of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloys. The former one shows excellent glass forming ability during rapid solidification⁽⁶⁾.

II. Experimental Procedures

Pure elemental powders of titanium (99.9%, 100 mesh), zirconium (98%, 100 mesh), copper (99.9%, 200 mesh) and nickel (99.9%, 250 mesh) were premixed thoroughly to get the required $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ (at%) compositions before milling. MA was carried out in a low energy milling machine. A 1.7 liter stainless steel vial with an inner diameter of 128 mm was utilized. The revolution speed of the vial was 95 ± 1 rpm. The ball-to-powder weight ratio used was 100:1, the total weight of the starting powders being 36 g. Prior to

milling, two weight percent of methanol was loaded in the milling vial to reduce the adherence of powders on the balls and the inner surface of the milling vial. The loading and the removing of powders were done in an argon-filled glove box in which the oxygen concentration was kept below 1.0 ppm. The structural evolution in the as-milled powders was examined by the following techniques: X-ray diffraction (XRD) on an M18X Model No. 1180 (Mac Science) X-ray diffractometer with Cu K α radiation; scanning electron microscopy (SEM) on an ABT-55 scanning electron microscope; differential scanning calorimeter (DSC) on a Shimadzu DSC50; JEOL JSM-6300 EDAX system for the chemical composition analysis as well as transmission electron microscopy (TEM) on an H-800 transmission electron microscope which was operated at an accelerating voltage of 200 kV. Samples for TEM observations were prepared by dispersing mechanically alloyed powders onto carbon coated copper meshes.

III. Experimental Results

1. MA of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy

Figure 1 shows the XRD patterns of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ powder samples before and after various milling periods up to 100 h. One can clearly see that, after milling for 4.5 h, (002) diffraction peak of Zr (at around 35 degrees) remained strong, while (100) peak of Zr (at around 32 degrees) almost disappeared. This may be due to the heavy deformation of Zr crystal during the early stage of milling. At the same time, a very similar result was observed in Ti. After milling for 10 h, all the diffraction

peaks corresponding to Ti, Zr, Cu and Ni became wide and weak due to the grain size refinement and the introduction of internal stress during milling. After milling for 50 h, an amorphous-like peak was seen in the XRD profile at around 40 degrees with a small crystalline peak at around 32 degrees. Further milling lead to a little change of the XRD pattern compared with that of the 50-h milled sample. So under the present milling condition, a mixture of amorphous and a small amount of crystallites was obtained in the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy. On the other hand, one can clearly see that no intermetallic compounds or metastable phases other than amorphous were detectable by XRD in all the as-milled samples, indicating that the interdiffusion of Ti, Zr, Cu and Ti atoms during milling may directly lead to an amorphous phase containing four elements under the present milling conditions.

Thermal stability of the as-milled powders was studied by using a differential scanning calorimeter. Figure 2 illustrates the DSC traces of samples milled for different times. During the DSC experiments, the samples were kept under a constant flow of argon gas. All the DSC curves were recorded at the same heating rate of 20 K/min using copper pans. From Fig. 2, one can see that in all samples examined, broad exothermic peaks were observed in the temperature range of 473–773 K on DSC curves. For the samples milled for 50 h and 100 h, other exothermic peaks appeared at about 873 K. In order to check whether or not all the exothermic peaks in Fig. 2 were related to structural evolution occurring in the samples upon heating, further detailed research was done as following.

Figure 3 presents the XRD results of the 100 h milled sample after heating to two characteristic temperatures on DSC (for 803 K see the arrow in Fig. 2). One can see that, at 803 K, no crystallization occurred in the sample compared with the as-milled state. So the broad exother-

Fig. 1 XRD patterns of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ samples milled for various times.

Fig. 2 Dynamic DSC curves of as-milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ samples recorded at a heating rate of 20 K/min.

Fig. 3 XRD patterns of the 100 h milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ sample after heating to different temperatures.

mic peak between 473 and 720 K and the sharp peak at about 780 K on the DSC curve in Fig. 2 were associated with the structural relaxation of the powder sample during heating. Such an obvious relaxation process prior to crystallization of the as-milled powder sample was not observed in the as-quenched amorphous sample of the same chemical composition⁽⁶⁾. When the temperature went up to 973 K, many complicated crystalline peaks were clearly visible (see Fig. 3). Thus, the exothermic peaks at around 873 K on DSC curves (see Fig. 2) of 50-h and 100-h milled samples were due to crystallization of the amorphous phase. The peak temperature of crystallization for the 100-h milled sample was 922 K. The index of these crystalline peaks in Fig. 3 is now in progress.

Figure 4(a) gives a dark field TEM image of the 25-h milled sample. Under this milling condition, a nanocrystalline sample with an average grain size of about 20 nm was obtainable. The 100-h milled sample was also subjected to TEM observation. A dark field image and its corresponding selected area electron diffraction (SAED) pattern were respectively presented in Figs. 4(b) and (c). The SAED pattern shows complicated diffraction rings because the amorphous phase superimposes onto nanocrystallites. However, we caught some amorphous particles by TEM as shown in Fig. 5. The above results confirms the partially amorphous nature of the 100-h-milled sample, which agrees well with the XRD results presented in Fig. 1.

The as-milled powders were also examined by SEM to check the powder morphology change during MA. Some SEM pictures were chosen in Fig. 6. In the early stage of milling, the powders were heavily cold rolled as illustrated by flattened particles in Fig. 6(a). On further milling,

the flattened particles began to be fractured into small pieces and the small pieces were cold welded onto the large flattened particle (see Fig. 6(b)). In the 35-h milled sample (Fig. 6(c)), many small fractured particles were attached to a large flattened particle. At this time, the particles were very heterogeneous. After milling for 50 h, amorphous was formed in the sample. Contrary to Fig. 6(c), an aggregation of nearly spherical, homogeneous particles was observed in the 50-h milled sample (Fig. 6(d)). A similar particle morphology was noticed in the 100-h milled sample as shown in Fig. 6(e).

It was found⁽¹⁸⁾ that the layered structure (flattened par-

Fig. 4 Dark field TEM images of 25-h milled (a) and 100-h milled (b) $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ samples and (c) the corresponding SAED pattern of Fig. 4(b).

Fig. 5 Bright field TEM image of 100 h milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ sample and its corresponding SAED pattern.

ticles) favoured the diffusion of different types of atoms because they contacted with clean surfaces with one another. The atomic diffusion could be further enhanced by long time milling, and a homogeneous phase was formed through gradual diffusion of thin layers. In the present case, 50 h milling lead to formation of an amorphous phase in the Ti–Zr–Cu–Ni sample. Prior to amorphization, one can see that deformation of powders was very serious, characterized by the flattened particles in Figs. 6(a) and (b). At that time the interdiffusion among the four elements was violent. This process can be greatly improved by the cold-welded structure of the small pieces of layered particles as seen in Fig. 6(c). After amorphization has occurred in the sample, the particles tend to become homogeneous as shown in Figs. 6(d) and (e).

2. MA of the eutectic composition of $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloy

In the study of bulk amorphous formation of the Ti–Zr–Cu–Ni system, Lin *et al.*⁽⁶⁾ found that $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloy can not be cast to 0.5-mm thick amorphous strips though its composition is quite near the quaternary eutectic point. However, $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy, whose composition is off the quaternary point, can be cast to 4-mm thick amorphous strips. So, MA of $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloy and a comparison with the results of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy as described earlier may allow a further investigation

of the amorphization mechanism of Ti–Zr–Cu–Ni alloy by MA. For this purpose, pure elemental powders of Ti, Zr, Cu and Ni corresponding to the composition of $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ were subjected to MA using the same milling machine and the same milling conditions. The XRD patterns of the as-milled samples were presented in Fig. 7. Comparing Fig. 7 with Fig. 1, one can find some common features between the MA process of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloys. Namely, no intermetallic compound was detectable throughout the whole milling process and the final product (after 100 h of milling) was a mixture of amorphous and a small amount of crystallites. Figure 8 compares the XRD results of the two alloys milled for 35 h. Obviously, amorphization by MA is easier to occur in the $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloy than in the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy, in contrary to the former melt quenching result. That means the easy glass forming ability by rapid quenching can not be directly related to a short milling time of MA. So, one cannot apply the theory of rapid quenching to predict the glass forming ability by MA.

Easy glass forming ability in the $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloy by MA may mean some special structure change during milling. Figure 9 shows some SEM images of $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ samples milled for different times. One can clearly see the flattened particles in the 4.5-h milled sample (Fig. 9(a)). When milled for 10 h, the flattened particles were fractured into small pieces and these pieces were cold-welded together to form some large agglomerates as seen in Fig. 9(b). However, when milled for 35 h, only large, nearly spherical particles were observed in Fig. 9(c). In the 100-h milled sample, the particle morphology is similar to the 35-h milled sample in Fig. 9(c). As presented in Fig. 6(c), one can see that some large flattened particles still remained in the 35-h milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ sample. At that time, no amorphous phase was formed in the sample. However, in the 35-h milled $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ sample as seen in Fig. 9(c) no such flattened particles were visible, likely due to the amorphization occurring in the $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ sample.

Thermal stability of the 100-h milled $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ sample was studied by DSC as shown in Fig. 10. The broad exothermic peak between 373 and 773 K on the DSC curve is due to structural relaxation in the sample upon heating, whereas the exothermic peak at around 873 K is due to the amorphous crystallization. The crystallization peak temperature was indexed to be 863 K. The XRD pattern of the 100-h milled $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ sample after heating to 973 K on DSC revealed the same crystalline peaks as those of the DSC scanned $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ sample in Fig. 7.

IV. Discussion

The foregoing investigations showed that the MA process of elemental Ti, Zr, Cu and Ni powder mixtures corresponding to compositions of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ can be described in the following scheme: μm -sized (Ti, Zr, Cu, Ni) $\rightarrow$ nm-sized (Ti, Zr,

Fig. 6 SEM pictures of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ samples milled for 4.5 h (a), 10 h (b), 35 h (c), 50 h (d) and 100 h (e).

Fig. 7 XRD patterns of $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ samples milled for different times.

Fig. 8 XRD patterns of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloys after 35 h of milling with a ball-to-powder weight ratio of 100:1.

Fig. 9 SEM pictures of $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ samples milled for 4.5 h (a), 10 h (b), 35 h (c) and 100 h (d).

Fig. 10 Dynamic DSC curve of the 100-h milled $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ sample. The heating rate is 20 K/min.

Cu, Ni) → amorphous + a small amount of nm-sized crystallites.

No intermetallic compounds were detectable in the whole milling process up to 100 h. After milling for 4.5 h, one of the diffraction lines of Zr, 100, almost disappeared as seen in Figs. 1 and 7. This may be due to the formation of textured Zr induced by heavy plastic deformation during the early stage of milling. Further investigation on this phenomenon is in progress. In the mechanical milling of pure Zr metal powders, we observed a very similar result⁽¹⁹⁾. The small crystalline peak beside the wide amorphous peak in Fig. 1 is now under investigation. One point we should address is that in the methanol-free sample we also observed a very similar

phenomenon. Further DSC measurements of both methanol-addition and methanol-free samples revealed almost the same exothermic peaks on DSC curves. That is to say, the small crystalline peak was not caused by the addition of 2 mass% of methanol. Chen *et al.*⁽²⁰⁾ proposed that ball-milling can stabilize two-phase states (amorphous + crystalline). The fraction of amorphous depends on the milling temperature and the milling intensity I . $I = M_b V_{\max} f / M_p$, where M_b is the mass of the ball, $V_{\max}$ the maximum velocity of the ball, f the impact frequency, and M_p the mass of powder in the vial. Only if the milling intensity I is increased above a threshold value, a fully amorphous state can be obtained. For this reason, we tried long time milling of $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy up to 300 h and tried milling under different ball-to-powder mass ratios from 50:1 to 300:1. However, no fully amorphous state was achieved in either condition. Maybe we have to use a high-energy milling machine.

The amorphization mechanism of MA has not yet been fully understood on the atomic scale due to the involvement of complicated nonequilibrium processes. Some empirical models have been proposed for predicting the glass-forming ability (GFA). Yermakov *et al.*⁽²¹⁾ explained amorphization during MA in terms of local melting and subsequent rapid solidification. However, no evidence of melting was seen in any of the amorphization experiments. Two prerequisite conditions, *i.e.*, negative enthalpy of mixing and widely differing diffusivities were proposed by Schwarz *et al.*⁽¹⁴⁾ for amorphization during MA. However, many exceptions have been reported later⁽²²⁾. It was generally considered⁽¹⁸⁾ that an increased

amount of lattice defects introduced during MA may raise the free energy of the system. Meanwhile, the fresh surfaces created by the repeated deformation process during MA were likely to supply an energetically favored site for the solid state reaction. Galy *et al.*⁽²³⁾ found that in the ball-milling process of NiZr_2 a fully nanocrystalline structure was achieved prior to amorphization. They suggested that amorphization occurs by chemical disordering at interfaces, induced by the scattering of shear waves. In the present case, four kinds of pure elements were involved in the MA process. Owing to the fact that no intermetallic compounds were detectable throughout the whole milling process, it seems that with four kinds of elements involved in MA the compositional fluctuation required for the nucleation of a crystalline phase during milling may be difficult to achieve so that the formation of a homogeneous amorphous phase containing four elements is much more preferential than the formation of any other phase.

For most of the as-quenched amorphous alloys, their crystallization temperatures are usually at around $0.5T_m$ (T_m is the melting point of the amorphous alloy in K). Another important factor affecting the thermal stability of the as-quenched amorphous is the quenching conditions. That is to say, cooling rate must be high enough to avoid visible nuclei in the as-quenched alloy because the crystallization temperature can be substantially decreased by the existence of quenched-in nuclei as a result of a lower cooling rate. Lin *et al.*⁽⁶⁾ reported that the crystallization peak temperature of the as-cast bulk amorphous $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy is 725 K. In our present case, the 100-h milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ sample shows an exothermic peak corresponding to amorphous crystallization at 922 K, which is almost 200 K higher than that of the as-cast sample. The analyzed composition of the 100-h milled sample is $\text{Ti}_{30.8}\text{Zr}_{8.4}\text{Cu}_{46.7}\text{Ni}_{8.1}\text{O}_{6.0}$ (at%). Compared with the nominal composition of the starting sample, 6.0 at% of oxygen was mixed into the 100-h milled sample. The intrinsic reasons for the thermal stability of the present as-milled powders need to be further identified. Merk *et al.*⁽²⁴⁾ found that the ball-milled $\text{Ni}_{55}\text{Zr}_{45}$ amorphous phase exhibited higher crystallization temperature and higher activation energy for crystallization than those of the melt-spun ribbons with the same chemical composition. Fukunaga *et al.*⁽²⁵⁾⁽²⁶⁾ studied and compared the microstructures of amorphous $\text{Ni}_{24}\text{Ti}_{76}$ alloys prepared by melt quenching and mechanical alloying. It was found that the bonding of unlike atoms in the as-milled amorphous state was much stronger than that in the liquid quenching amorphous state. This atomic arrangement may contribute to the thermal stability of the as-milled amorphous. In the as-milled $\text{Cu}_x\text{Ti}_{100-x}$ amorphous alloys, Nagumo *et al.*⁽²⁷⁾ found that the Cowley CSRO parameter showed a monotonic decrease with increasing Cu concentration. That is to say, the Cowley CSRO parameter changed from positive ($x < 68$) to negative ($x > 68$). However, in the as-quenched Cu-Ti amorphous alloys the CSRO parameter is negative for all compositions. The above experimental results demonstrated

that the microstructure of the as-milled amorphous phase can be different from that of the as-quenched amorphous counterpart with the same chemical composition. Anyway, the high thermal stability of the as-milled powders in the present case compared with the as-quenched alloy is of practical significance.

The glass forming ability by MA has been discussed by Schultz⁽²⁸⁾ using a free energy diagram. He found a wide glass-forming range in the central part of the phase diagram. The eutectic compositions of the equilibrium phase diagram do not play a role during MA. Further experiments on MA of several binary alloy systems⁽¹³⁾⁻⁽¹⁵⁾⁽²⁹⁾ confirmed the above prediction. Our experimental results on MA of two quaternary Ti-Zr-Cu-Ni alloys showed that the amorphization mechanisms induced by MA and by rapid quenching were completely different. Amorphization by MA is a solid-state reaction process, which may result in a different amorphous structure from that of the traditional as-quenched amorphous phase. From this viewpoint, the difference in the crystallization temperature between the as-quenched and the as-milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloys may be understandable.

V. Conclusions

(1) The MA process of elemental powder mixtures of Ti, Zr, Cu and Ni corresponding to both $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ (at%) can be described as following: μm -sized (Ti, Zr, Cu, Ni) $\rightarrow$ nm-sized (Ti, Zr, Cu, Ni) $\rightarrow$ amorphous + a small amount of nm-sized crystallites. No intermetallic compound or other metastable phases was detectable prior to amorphization in the whole milling process. After 100 h of milling, a mixture of both amorphous and nanocrystallites was obtainable in the above two alloys. The analysed chemical composition of the 100-h milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ sample is $\text{Ti}_{30.8}\text{Zr}_{8.4}\text{Cu}_{46.7}\text{Ni}_{8.1}\text{O}_{6.0}$ (at%).

(2) The 100-h milled $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ powder sample shows a crystallization temperature which is about 200 K higher than the reported value of the liquid-quenched alloy with the same chemical composition.

(3) Amorphization is easier to occur in $\text{Ti}_{37}\text{Zr}_{17}\text{Cu}_{42}\text{Ni}_4$ alloy than in $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy during MA, which is contrary to the traditional rapid quenching technique. That is to say, the easy glass forming ability by rapid quenching can not simply mean a short milling time by MA.

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