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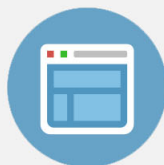
Formation of an amorphous phase and its crystallization in the immiscible Nb–Zr system by mechanical alloying

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Mechanical alloying of binary Nb-Zr powder mixtures was carried out to evaluate the formation of metastable phases in this immiscible system. The milled powders were characterized for their constitution and structure by X-ray diffraction and transmission electron microscopy methods. It was shown that an amorphous phase had formed on milling the binary powder mixture for about 10 h and that it had crystallized on subsequent milling up to 50–70 h, referred to as mechanical crystallization. Thermodynamic and structural arguments have been presented to explain the formation of the amorphous phase and its subsequent crystallization. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4825325]

I. INTRODUCTION

Amorphous alloys or metallic glasses have an interesting combination of physical, chemical, mechanical, and magnetic properties and have found many applications.[1–3] These alloys have been produced in several alloy systems by non-equilibrium processing methods such as rapid solidification processing of liquid alloys involving solidification rates of as high as 10^6 K/s,[4] vapor deposition, where the quenching rates can be even higher, typically 10^{12} K/s,[5] mechanical alloying,[6,7] ion beam mixing,[8] and others.[9] Majority of these metastable alloys have been produced by liquid quenching or vapor quenching methods in alloy systems that show a negative heat of mixing, since, only under this condition, the constituent elements mix thoroughly in the liquid or vapor phases. But, when the heat of mixing is positive, constituent elements cluster together and no alloying occurs. Consequently, there have not been any reports of amorphous phase formation in alloy systems that show a positive heat of mixing. However, alloys produced by severe plastic deformation methods such as mechanical alloying (MA) and ion beam mixing (IBM) (which involves large displacements of atomic positions due to irradiation) do not follow phase diagram restrictions and consequently the type of metastable phases produced are significantly different from those produced by liquid quenching or vapor quenching methods, and include the amorphous phases in some of these alloy systems.

Nb–Zr alloys exhibit a positive heat of mixing, the magnitude of which has been reported to be anywhere between $+6$ and $+17$ kJ/mol.[10–12] These alloys are scientifically interesting since they exhibit interesting superconducting properties,[13] and these alloys also show the presence of metastable phases such as omega.[14] Jin *et al.*[10] showed that an amorphous phase could be produced in ion-irradiated multilayer thin films corresponding to the composition of Nb–40 at. % Zr. Further, through thermodynamic calculations and IBM of multilayered thin films, Wang *et al.*[12] have shown that an amorphous phase could be produced in the Nb–Zr system in the wide composition range of 8–88 at. % Zr. Most recently, Suryanarayana and Liu[11] showed that there were indications of formation of an amorphous phase in mechanically alloyed Nb–10 and 20 at. % Zr powder mixtures. To investigate whether an amorphous phase could be produced in other alloy compositions in the Nb–Zr system by MA and also to determine whether the effects of IBM and MA are similar, we decided to study the effects of MA on phase formation in Nb–40 to 50 at. % Zr alloy compositions.

II. EXPERIMENTAL PROCEDURE

Pure elemental powders of Nb and Zr (both of -325 mesh size and higher than 99.8% purity) were mixed in the proportion of 40, 45, and 50 at. % Zr (and the rest Nb) and milled in a Fritsch Pulverisette 5 planetary ball mill at a fixed rotation speed of 300 rpm and under argon atmosphere using tungsten carbide (WC) vials and WC grinding balls. A ball-to-powder weight ratio of 10:1 was used and milling was interrupted every 30 min for every 2.5 h of milling to minimize excessive heating of the powder. Further, the vials were opened every 5 h of milling to scrape the accumulated powder from the vial walls, which helped reduce the amount of unprocessed powders. To ensure reproducibility of the results, every experiment was repeated three times. No process control agent was added during the milling process to minimize powder contamination.

The milled powders were characterized for the constitution and structure of the phases using X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods. XRD was conducted using a Bruker (AXSD-8) machine with Cu Kα radiation. An FEI TEM operating at 200 keV was used to unravel the presence of different phases. The

homogeneity of the synthesized alloy powder during MA process was verified using energy dispersive spectroscopy.

III. RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of the Nb–40 at. % Zr powder blend as a function of the milling time. The as-blended powder shows the presence of elemental Nb and Zr only and no other phase is present. On milling the powder, the intensities of the diffraction peaks of both the metals decreased and their widths increased due to a reduction in crystallite size and introduction of lattice strain.[6,7] However, on continued milling of the powder blend to about 10 h, the diffraction peaks were replaced by a broad diffuse halo, corresponding to the (110) peak of Nb, suggesting that an amorphous phase had partially formed. The fraction of the amorphous phase increased with milling time reaching a maximum of about 60 vol. % on milling the powder for 30–40 h. However, on continued milling to 50–70 h, a crystalline phase had formed suggesting that the amorphous phase had crystallized due to milling, a phenomenon that has been termed mechanical crystallization.[15–17] A similar trend was noted on milling the powder blends of other compositions as well, even though the times for the amorphous phase formation were different. The trend was that the time for amorphization decreased with an increase in the Zr content in the powder blend. This can be rationalized on the basis that Nb has a higher melting temperature than Zr and therefore the time required for amorphization increased with increasing Nb content. Further, the thermal stability of this amorphous phase is also expected to be higher because of the increased melting temperature of the alloy with increasing Nb content.

Figure 2 shows TEM micrographs and selected area diffraction patterns of the Nb–40 at. % Zr powder blends milled for 10 and 70 h. Some regions in the powder milled for 10 h
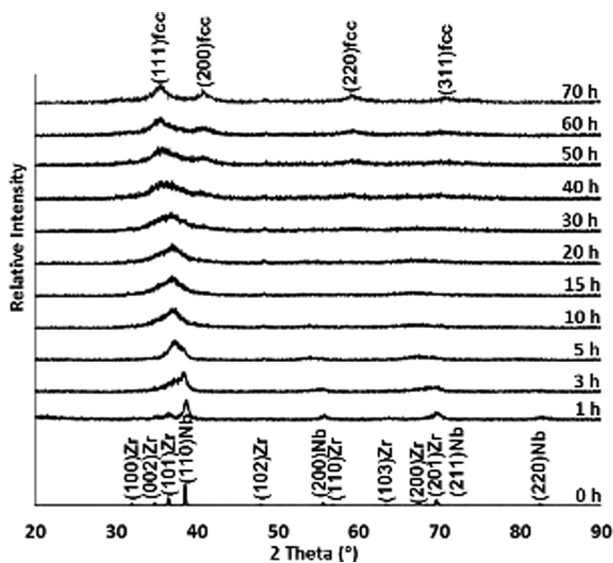

FIG. 1. X-ray diffraction patterns of the Nb–40 at. % Zr powder blend milled for different times. While the starting (unmilled powder) showed only the diffraction peaks from both Nb and Zr, the milled powder showed a decrease in peak intensity and an increase in peak width due to reduction in crystallite size and introduction of lattice strain. An amorphous phase started to form on milling the powder for about 10 h, and its volume fraction increased with increasing milling time. On milling the powder for 50–70 h, a crystalline fcc phase had formed.

clearly showed the presence of an amorphous phase. This is confirmed from the high-resolution TEM micrograph that shows the salt-and-pepper like contrast (Fig. 2(a)) and the presence of a broad diffuse halo in the diffraction pattern (Fig. 2(b)). This observation clearly confirms that it has been possible to produce an amorphous phase in this immiscible Nb-Zr system. But, the electron micrograph of the powder milled for 70 h clearly shows the presence of lattice fringes suggesting that a crystalline phase is present at this stage (Fig. 2(c)) and the diffraction pattern (Fig. 2(d)) clearly confirms the presence of a crystalline phase. From the position of the rings, this crystalline phase has been indexed to have an fcc structure with $a = 0.44$ nm. The formation of a crystalline phase on continued milling after the formation of the amorphous phase clearly suggests this could be due to mechanical crystallization, even though other possibilities exist.[17] Since no crystalline phase with an fcc structure exists in this alloy system under equilibrium conditions, it can be concluded that this is a metastable phase.

Let us now rationalize the present results in terms of known mechanisms of amorphous phase formation. There have been several instances of amorphous phase formation in alloys subjected to MA. Even though amorphous phases have been produced by other processes, it has been noted that the composition ranges for amorphous phase formation by MA are much wider than by other processes.[6,7] However, the criteria for amorphous phase formation have been shown to be different for liquid-quenching techniques such as rapid solidification processing[18,19] and solid-state processing techniques such as MA.[20] A common criterion observed for amorphous phase formation produced by all the techniques is that there should be a significant difference in atomic sizes between the constituent elements, which introduces strain into the alloy. It was shown[21] that, in a solid solution, the strain energy increases linearly with the solute content. When the lattice strain reaches a critical value, the glassy alloy becomes energetically more favorable than the corresponding crystalline phase. In other words, the strain introduced into the system destabilizes the crystal lattice resulting in the formation of the amorphous phase.[22] In fact, it was highlighted that "alloying makes glass formation easier, not because alloying stabilizes a glass, but because it destabilizes a crystal."[22] It was noted that the minimum solute concentration required to cause destabilization of the crystalline lattice in a binary alloy is obtained from the empirical relationship,[21]

$$\left[\left(\frac{r_B}{r_A} \right)^3 - 1 \right] \times C_B^{min} = 0.1,$$

where r_B and r_A represent the radius of the B (solute) and A (solvent) atoms, respectively, and C_B^{min} represents the minimum solute content required to form the amorphous phase. In the case of the Nb–Zr system, the radii of the Nb and Zr atoms are 0.146 and 0.158 nm, respectively, and accordingly C_B^{min} works out to be 0.374 or 37.4 at. % Zr. It may be noted that this value is very close to the value of 40 at. % Zr observed in this investigation.

By controlling the radiation dose in different Nb-Zr multilayer thin films, Wang et al.[12] were able to produce an amorphous phase in a wide composition range of 8–88 at. %
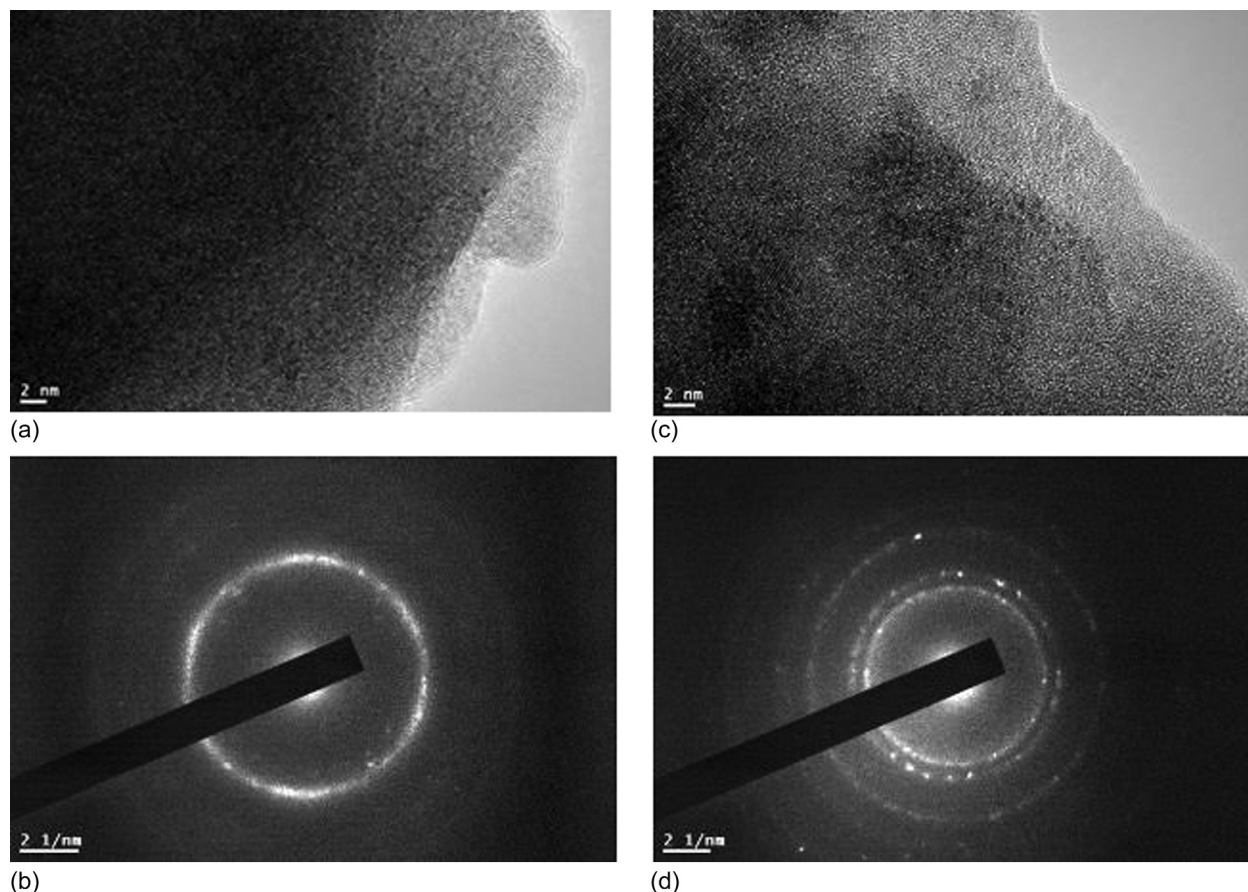
FIG. 2. Transmission electron micrographs and selected area diffraction patterns of the Nb-40 at. % Zr powder blends milled for 10 h and 70 h. The micrograph of powder milled for 10 h (a) shows the presence of the amorphous phase, confirmed by the diffraction pattern showing a halo (b), while the micrograph of powder milled for 70 h (c) shows the presence of the fcc crystalline phase, confirmed from the diffraction pattern (d).

Zr, attributed to the increased added energy to the system. Thus, it appears possible to obtain the amorphous phase in different composition ranges by adjusting the processing parameters even during the MA processing.

An exhaustive review of the literature on formation of metastable phases, including amorphous phases, in immiscible systems has been presented by Ma.[23] It was noted that amorphization was possible even in alloy systems that exhibited positive heat of mixing. These systems include Ag-Cu,[24] Cu-Nb,[25] Cu-Ta,[26,27] among other immiscible systems. In all these alloy systems, an amorphous phase is produced through mechanically-driven solid–state amorphization methods, e.g., cold rolling or cold drawing of multilayer thin films. An important point to be noted is that, in all these systems, amorphization has been only partial and that a homogenous amorphous phase was never obtained. For example, the amorphous phase is observed only at the Cu/Nb interfaces in the Cu-Nb system[25] and in localized regions in the Ag-Cu system.[24] In majority of the cases, formation of the amorphous phase was confirmed only through XRD experiments. It is possible that these are only "X-ray" amorphous and additional experiments such as TEM and calorimetric measurements could help in determining whether these phases are truly amorphous. This is because the broad peaks in XRD patterns could result from (i) extremely fine crystalline grain structures or (ii) very fine crystals distributed

uniformly inside an amorphous matrix.[7] But, in the present investigation, we were able to confirm the presence of the amorphous phase through both XRD and TEM methods and therefore this lends more credibility to the reported result.

As mentioned earlier, formation of amorphous phases in immiscible alloy systems has been reported to occur through methods such as IBM, MA or cold rolling of multilayer films, but not through rapid solidification processing methods. In severe plastic deformation methods, a very large number of new surfaces and interfaces are created. This excess interfacial energy provides the driving force for amorphization, because it raises the free energy of the system containing the crystalline phases (solid solutions or intermetallics) to above that of the hypothetical amorphous phase. In fact, thermodynamic calculations using the Miedema's model[28] or Alonso's method[29] clearly confirm this speculation.

It was also mentioned that a crystalline phase had formed on continued milling after the amorphous phase had formed. There have been several reports of similar observations.[15–17] The crystalline phase could be a metastable or equilibrium phase formed as a result of decomposition of the amorphous phase or it could be a contaminant phase. The technique of MA could always introduce contamination into the milled powder due to wear and tear of the grinding medium, use of a process control agent, or atmospheric contamination. Chemical analysis of the milled powder showed

that there was only some slight contamination. For example, the carbon and nitrogen contents were zero on milling the powders for 10 h, but they increased to 0.28 and 2.80 wt. %, respectively, on milling the powders to 30 h. With continued milling up to 70 h, these values increased to 0.42 and 6.52 wt. %, respectively. The powder milled for 70 h also showed the presence of about 1.1 wt. % W. The presence of W and C in the milled powder can be attributed to the use of very hard WC vial and balls, which show much less wear and tear than stainless steel balls, which are much softer than those of WC. Also, IBM of multilayer thin films will not have contamination during processing. Since these films subjected to IBM also showed the presence of two metastable crystalline phases, both having the fcc crystal structure,[10] we can conclude that the amorphous phase had crystallized to form a metastable crystalline phase and that contamination may not be the reason for the formation of the crystalline phase in our case. Further, in the IBM case, the lattice parameter of the Nb-rich Nb-19 at. % Zr fcc phase was reported to be 0.435 nm, while that of the Zr-rich Zr-32 at. % Nb fcc phase was 0.440 nm. In our alloy with Nb-40 at. % Zr, the lattice parameter was 0.44 nm, very close to the value reported earlier in IBM alloys. Thus, it is safe to infer that this fcc phase is not a contaminant phase, but that which has formed as a result of crystallization of the amorphous phase. The reasons for the formation of the crystalline phase on continued milling of the amorphous phase have been detailed earlier.[17] The lowered free energy of the system consisting of a mixture of amorphous and crystalline phases, in comparison to an amorphous phase, has been shown to be the reason for the crystallization of the amorphous phase. It may be appropriate to mention here that if the milled powders containing the amorphous phase (at 10 h) and the metastable crystalline phase (at 70 h) are annealed at reasonably high temperatures, they are likely to result in the formation of the equilibrium phases, which in the present case will be a mixture of Nb and Zr, since they are immiscible under equilibrium conditions.

IV. CONCLUSIONS

An amorphous phase was synthesized in mechanically alloyed Nb-Zr alloys that show a positive heat of mixing between the constituent elements. The composition range in which the amorphous phase had formed was rationalized in terms of the lattice strain introduced into the alloy system. On continued milling of the powder containing the amorphous phase, a crystalline phase had formed that had an fcc structure. These results are somewhat similar to those obtained by ion beam mixing suggesting that these two methods produce similar types of metastable phases. However, an important difference was that the amorphous phase had crystallized on continued milling.

[1]*Rapidly Solidified Alloys*, edited by H. H. Liebermann (Marcel Dekker, New York, 1993).
[2]T. R. Anantharaman and C. Suryanarayana, *Rapidly Solidified Metals: A Technological Overview* (Trans Tech Publications, Zurich, 1987).
[3]*Glassy Metals III*, edited by H. Beck and H.-J. Güntherodt (Springer-Verlag, Berlin, 1994).
[4]W. Klement, R. H. Willens, and P. Duwez, Nature **187**, 869–870 (1960).
[5]D. M. Mattox, *Handbook of Physical Vapor Deposition (PVD) Processing* (Noyes Publications, Westwood, NJ, 1998).
[6]C. Suryanarayana, Prog. Mater. Sci. **46**, 1–184 (2001).
[7]C. Suryanarayana, *Mechanical Alloying and Milling* (Marcel Dekker, New York, 2004).
[8]B. X. Liu, W. S. Lai, and Z. J. Zhang, Adv. Phys. **50**, 367–429 (2001).
[9]C. Suryanarayana, *Non-Equilibrium Processing of Materials* (Pergamon, Oxford, 1999).
[10]O. Jin, Z. J. Zhang, and B. X. Liu, J. Appl. Phys. **78**, 149–154 (1995).
[11]C. Suryanarayana and J. L. Liu, Int. J. Mater. Res. **103**, 1125–1129 (2012).
[12]T. L. Wang, S. H. Liang, J. H. Li, K. P. Tai, and B. X. Liu, J. Phys. D: Appl. Phys. **41**, 095310 (2008).
[13]A. Cavalleri, F. Giacomozzi, L. Guzman, and P. M. Ossi, J. Phys.: Condens. Matter **1**, 6685–6693 (1989).
[14]G. Aurelio, A. Fernandez Guillermet, G. J. Cuello, and J. Campo, Metall. Mater. Trans. A **32**, 1903–1910 (2001).
[15]M. L. Trudeau, R. Schultz, D. Dussault, and A. Van Neste, Phys. Rev. Lett. **64**, 99–102 (1990).
[16]U. Patil, S.-J. Hong, and C. Suryanarayana, J. Alloys Compd. **389**, 121–126 (2005).
[17]S. Sharma and C. Suryanarayana, J. Appl. Phys. **102**, 083544 (2007).
[18]C. Suryanarayana, I. Seki, and A. Inoue, J. Non-Cryst. Solids **355**, 355–360 (2009).
[19]C. Suryanarayana and A. Inoue, *Bulk Metallic Glasses* (CRC Press, Boca Raton, 2011).
[20]S. Sharma, R. Vaidyanathan, and C. Suryanarayana, Appl. Phys. Lett. **90**, 111915 (2007).
[21]T. Egami and Y. Waseda, J. Non-Cryst. Solids **64**, 113–134 (1984).
[22]T. Egami, J. Non-Cryst. Solids **205–207**, 575–582 (1996).
[23]E. Ma, Prog. Mater. Sci. **50**, 413–509 (2005).
[24]H. W. Sheng, G. Wilde, and E. Ma, Acta Mater. **50**, 475–488 (2002).
[25]X. Sauvage, L. Renaud, B. Deconiihout, D. Blavette, D. H. Ping, and K. Hono, Acta Mater. **49**, 389–394 (2001).
[26]G. Veltl, B. Scholz, and H. D. Kunze, Mater. Sci. Eng. A **134**, 1410–1413 (1991).
[27]J. Xu, J. H. He, and E. Ma, Metall. Mater. Trans. A **28**, 1569–1580 (1997).
[28]A. R. Miedema, A. K. Niessen, F. R. de Boer, R. Boom, and W. C. M. Mattens, *Cohesion in Metals: Transition Metal Alloys* (North Holland, Amsterdam, 1989).
[29]J. A. Alonso, L. J. Gallego, and J. A. Simozar, Nuovo Cimento **12**, 587 (1990).