Journal of Alloys and Compounds 434–435 (2007) 315–318

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Fabrication of Ti–Zr–Ni bulk quasicrystal by mechanical alloying and pulse current sintering

Akihiro Matsumoto*, Keizo Kobayashi, Toshiyuki Nishio, Kimihiro Ozaki

Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology,
2266-98 Anagahora Shimoshidami, Moriyama Nagoya 463-8560, Japan

Abstract

Elementary powder mixtures with the composition of Ti–45 at.%Zr–38 at.%Ni and Y as an additive has been mechanically alloyed using a planetary ball mill. All of the obtained powders consisted of mainly an amorphous phase. With increasing content of Y, the quantity of icosahedral quasicrystal increased in heat-treated powders. The addition of 3 at.%Y led to almost fully quasicrystalline phase. Ti–Zr–Ni bulk quasicrystal was successfully prepared using a pulse current sintering method under an applied pressure of 500 MPa at 813 K. The obtained bulk quasicrystal material has a Vicker hardness of 6.9 GPa.

Keywords: Amorphous materials; Quasicrystals; Mechanical alloying; Powder metallurgy

1. Introduction

Ti–Zr–Ni quasicrystalline phase has been mainly prepared by rapidly quenching, e.g. melt spinning technique [1]. However, it is difficult to process a reactive metal such as titanium owing to high reactivity with the crucible. Mechanical alloying (MA) is a powerful method of producing metastable materials such as amorphous and quasicrystalline powders. Ti–38 at.%Zr–17 at.%Ni metastable powder was prepared using MA and the subsequent heat treatment [2,3]. However, a single phase of icosahedral structure was not obtained by MA. In other words, $Ti(Zr)_2Ni$ phase inevitably coexisted with icosahedral quasicrystalline phase. Recently, we have successfully produced almost all icosahedral quasicrystalline powder by the addition of Y element [4].

Ti–Zr–Ni icosahedral quasicrystalline phase is expected as a novel hydrogen-storage material owing to the presence of more tetrahedral interstitial sites than in normal alloys [5]. However, the other properties, such as mechanical and electrical property, have not been clarified enough. If a bulk quasicrystal is produced, a novel application may be developed.

Foster et al. prepared a Ti–41.5 at.%Zr–17 at.%Ni quasicrystal with the dimension of 1.321 mm × 1.1 mm × 1.644 mm using arc melting [6]. Qiang et al. produced Ti–Zr–Ni quasicrystalline rod 6 mm in diameter and about 10 mm in length using suction-casting of the alloy melts in a water-cooled copper mold [7]. However, a casting technique always remains a problem, that is, a high reactivity with the crucible.

We have successfully produced an amorphous Ti–Si–Fe bulk material using pulse current sintering method of amorphous powder prepared by MA [8]. Pulse current sintering method enables us to prepare non-equilibrium materials owing to rapid sintering under high applied pressure. In this study, we have made an attempt to produce Ti–Zr–Ni bulk quasicrystalline materials using pulse current sintering of mechanically alloyed powder and investigated the mechanical property of the bulk quasicrystalline product.

2. Experimental detail

Titanium (99.9 mass%, −45 μm), zirconium (99 mass%, −45 μm), nickel (99.9 mass%, −7 μm) and yttrium (99.9 mass%, −150 μm) powders were used as starting materials for MA and mixed to give the desired composition of Ti–38 at.%Zr–17 at.%Ni with 0, 1 and 3 at.%Y. The powder mixtures were milled in a planetary ball mill at the rotation speed $2.83\ s^{-1}$ under an argon atmosphere of 66 kPa. The container ($5 \times 10^{-4}\ m^3$) and balls (0.01 m in diameter) made of hardened steel were used for milling. The milled powders were poured into a hard metal die, with 6 mm inner diameter and 20 mm outer diameter, and heated up to 853 K maximum in vacuum under an applied stress of 500 MPa using a pulse current sintering method. The consolidating temperature was measured using alumel–chromel thermocouple inserted 3 mm into the die. The structural evolution of the milled powders and compacts was examined by

---

* Corresponding author. Tel.: +81 52 736 7205; fax: +81 52 736 7202.
E-mail address: akihiro-matsumoto@aist.go.jp (A. Matsumoto).

0925-8388/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2006.08.192

X-ray diffraction analysis (XRD, Cu Kα). Transmission electron microscopy (TEM, 200 kV) was used for the microstructural observation. Vickers hardness test was carried out at a load of 5 kg at room temperature. Rectangular specimens measuring 1.5 mm × 1.5 mm × 3 mm were sectioned from the compacts using a multi wire saw, followed by mechanical polishing. They were deformed in compression at room temperature between two hard metal platens using an Instron-type testing machine at a strain rate of 1.0×10^{-3} s^{-1}.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of Ti–38 at.%Zr–17 at.%Ni powders with 1, 3 at.%Y addition prepared by MA for 720 ks. All of them were broadened at around $2\theta = 37°$. TEM observation confirmed a mainly amorphous phase with a small amount of nanosized Y or Y_2O_3 particles dispersed in it [4].

Fig. 2 shows X-ray diffraction patterns of Y-added Ti–38 at.%Zr–17 at.%Ni powders milled for 720 ks after the heat treatment at 813 K. Two intensity peaks of icosahedral quasicrystalline phase (hereafter i-phase) around 35–39° overlap each other with two peaks of $Ti(Zr)_2Ni$ phase (hereafter T-phase). Therefore, i-phase is clearly identified by 1 1 1 1 0 1 (at $2\theta = 44.16$) and 1 0 1 0 0 0 (at $2\theta = 64.59$), whereas T-phase is identified by 4 4 0 ($2\theta = 45.35$) and 6 6 0 ($2\theta = 66.07°$). 6 6 0 peak of T-phase is distinctly observed as well as 1 0 1 0 0 0 peak of i-phase for the non-additive powder. Peak intensity of 4 4 0 and 6 6 0 for T-phase obviously decreased with increasing Y content. XRD profile of 3 at.%Y addition powder was predominantly comprised of i-phase with a small amount of Y_2O_3. It has been reported that Ti_2Ni type phase stabilized with increasing content of oxygen [9]. To some degree, oxygen contamination in the milled powder cannot be avoided, because adsorbed oxygen and/or metal oxide on the surface of powder particle and residual oxygen in the milling atmosphere are inevitably incorporated. In fact, oxygen content of the milled powders was measured to be about 0.9 mass% using an inert gas fusion method.

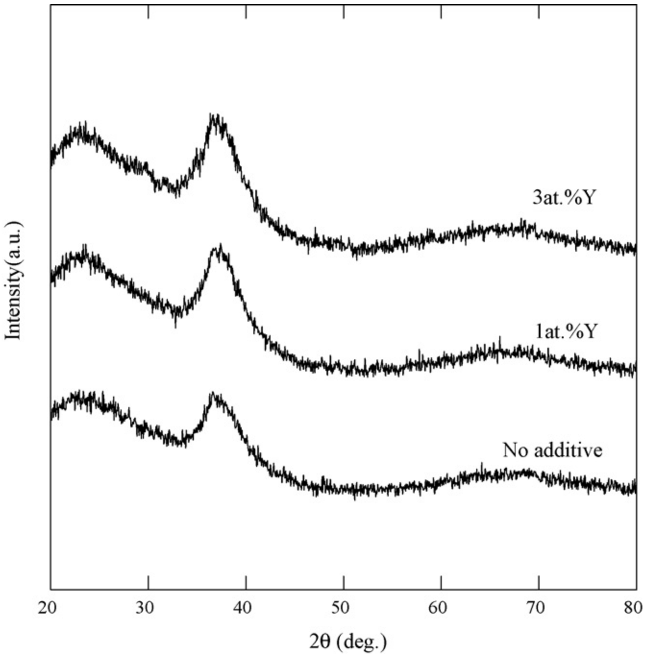

Fig. 1. X-ray diffraction patterns of Ti–38 at.%Zr–17 at.%Ni powders with no additive and Y addition prepared by mechanical alloying for 720 ks.

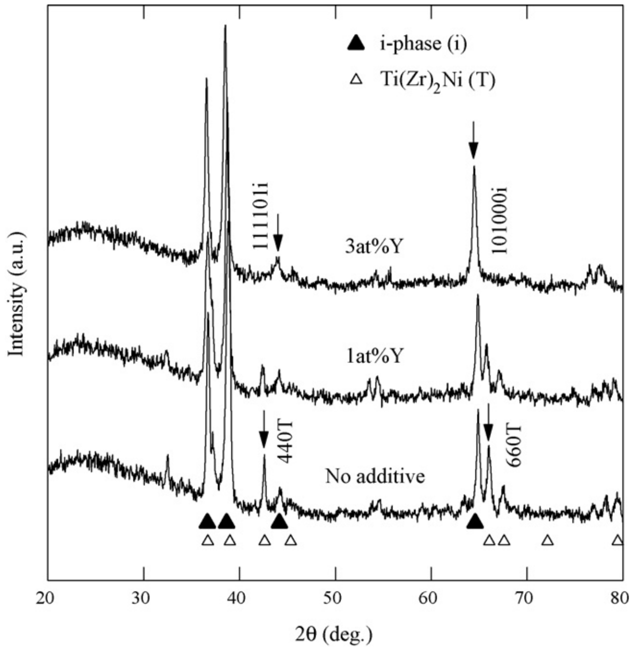

Fig. 2. X-ray diffraction patterns of Ti–38 at.%Zr–17 at.%Ni powders of Fig. 1 after the heat treatment at 813 K.

Fig. 3 shows the selected area diffraction pattern of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni powder after the heat treatment at 813 K revealing diffraction spots of Y_2O_3 2 2 2. The heat of mixing ΔH for Ti–O, Zr–O, Ni–O and Y–O are estimated to be $\Delta H_{Ti–O} = -315$ kJ/mol, $\Delta H_{Zr–O} = -366$ kJ/mol, $\Delta H_{Ni–O} = -120$ kJ/mol and $\Delta H_{Y–O} = -381$ kJ/mol [10]. In other words, yttrium oxide (Y_2O_3) is the most stable oxide among them. Therefore, the heat treatment of the Y-added powder leads to the formation of Y_2O_3 because Y has a higher affinity with oxygen than Ti, Zr and Ni. This resulted in preventing the formation of $Ti(Zr)_2Ni$ type phase in terms of reduction of oxygen content in the amorphous matrix, leading to the drastic increase in an icosahedral quasicrystalline phase.

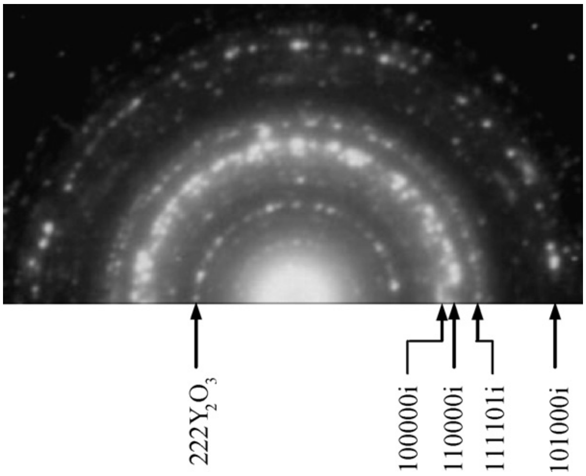

Fig. 3. Selected area diffraction patterns of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni powder of Fig. 2.

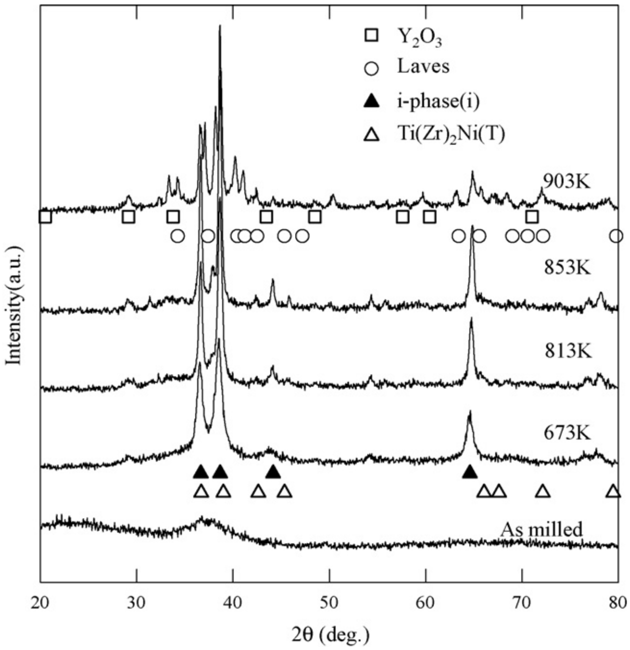

Fig. 4. X-ray diffraction patterns of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni powders prepared by mechanical alloying for 720 ks after the heat treatment at various temperatures.

Fig. 4 shows the X-ray diffraction patterns of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni powder after the heat treatment at various temperatures. I-phase was dominant for the sample heat-treated at 673 and 813 K. T-phase and Laves phase (C14 hexagonal) appeared at higher temperatures [11]. Therefore, it is necessary to consolidate the milled powder at the temperature lower than 813 K to prepare a bulk quasicrystalline specimen. An attempt to consolidate 3 at.%Y-added powder was made using a pulse current sintering technique. For comparison, the grinded powders (−90 μm) of Ti–38 at.%Zr–17 at.%Ni ribbon prepared by rapidly quenching (RS powder) was consolidated in the same way.

Fig. 5 shows the relationship between the temperature and shrinkage of the powder specimen under a pressure of 500 MPa. RS powder expanded with increase in temperature up to 700 K. RS specimen began to shrink at around 700 K and the shrinkage did not stop at even 813 K. On the contrary, MA specimen shrank gradually with an increase in temperature and the shrinkage stopped at 803 K. The change of the slope at 630 K is probably due to transformation from amorphous to quasicrystalline phase. The MA compact was fully dense, while the RS compact contained a small amount of pore with a size of 2–5 μm. It is conjectured that the excellent compactability of the milled powder is due to viscous flow of amorphous phase and grain boundary slip during nanoquasicrystallization.

Fig. 6 shows the relationship between the consolidating temperature and porosity of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni compacts. With increasing the applied pressure to the powder specimen, the temperature necessary to prepare a dense compact decreased. The heat-treated specimen at 813 K was predominantly comprised of i-phase, while T-phase and Laves phase appeared at 853 K. Therefore, it is necessary to consolidate the milled powder under a pressure of 500 MPa at less than 853 K to obtain a dense icosahedral bulk quasicrystalline specimen.

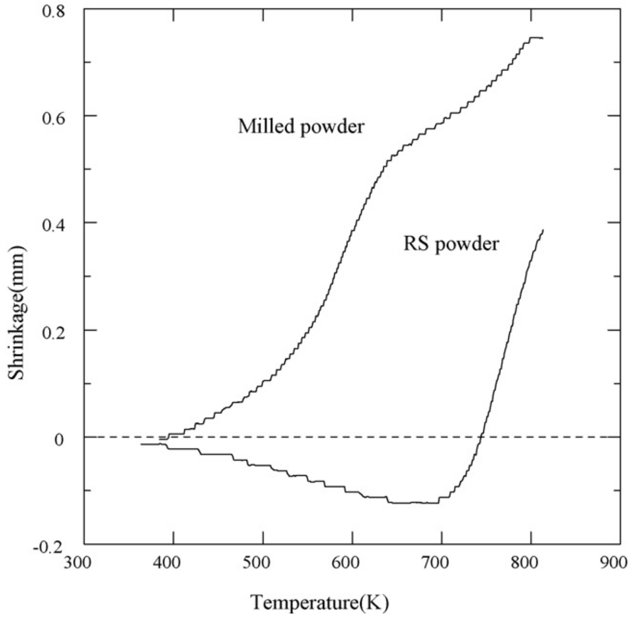

Fig. 5. The relationship between the temperature and shrinkage of the powder specimens under a pressure of 500 MPa.

Fig. 7 shows a bright field TEM image and selected area diffraction pattern for 3 at.%Y-added Ti–38 at.%–17 at.%Ni compact prepared under a pressure of 500 MPa at 813 K. The structure shows icosahedral quasicrystalline grains with a small amount of dispersed nanosized Y_2O_3. Vickers hardness and the compressive strength were 6.9 GPa and 650 MPa, respectively. Yi et al. prepared a Ti–41.5 at.%Zr–17 at.%Ni bulk sample that has nanosized (i + α) two-phase microstructure (α:Ti solid solu-

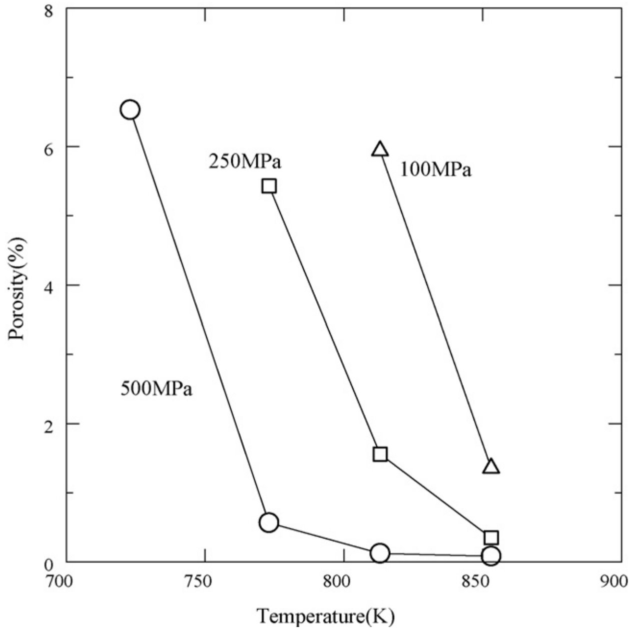

Fig. 6. The relationship between the temperature and porosity of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni compacts when the applied pressure was varied.

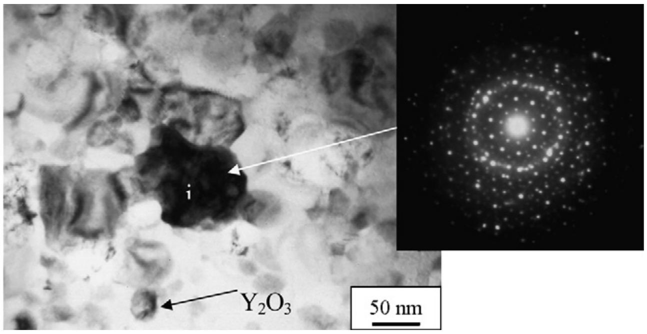

Fig. 7. Bright field image and selected area diffraction pattern of a grain of 3 at.%Y-added Ti–38 at.%–17 at.%Ni compacted at pressure of 500 MPa and 813 K.

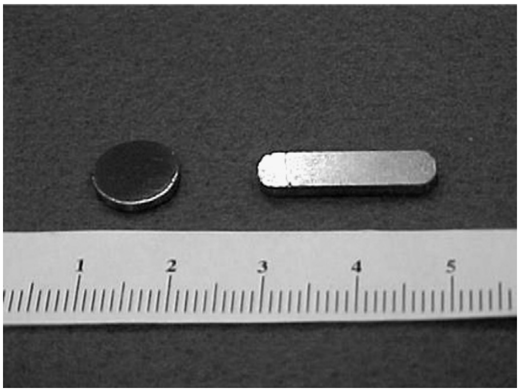

Fig. 8. Appearance of the samples of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni compacts prepared by mechanical alloying and pulse current sintering.

tion) by mechanical alloying and hot pressing at 803 K under a pressure of 1000 MPa [12]. The hardness of the two phases compact was 6.2 GPa. The hardness of Ti–38 at.%Zr–17 at.%Ni compact in the present study is reasonable because it has almost all quasicrystalline structure. The specimen subjected to compression was fractured into pieces at maximum load with no deformation. The specimen is nanostructured, so it is difficult to assure that the mechanical test results show an intrinsic nature of the icosahedral quasicrystal. Further study is needed to clarify the mechanical property of the icosahedral phase.

Fig. 8 shows the appearance of 3 at.%Y-added Ti–38 at.%Zr–17 at.%Ni compacts with circular and rectangular shapes. They were successfully consolidated with no cracks by mechanical alloying and pulse current sintering. Therefore, the combined process enabled us to produce dense bulk quasicrystalline Ti–Zr–Ni with various shapes.

4. Conclusion

Mechanical alloying of Y-added Ti–38 at.%Zr–17 at.%Ni powder produced mainly an amorphous structure. Y addition led to an increase in icosahedral quasicrystalline phase for Ti–38 at.%Zr–17 at.%Ni specimen, because the formation of Y_2O_3 diminished the oxygen content in Ti–Zr–Ni matrix and prevented formation of $Ti(Zr)_2Ni$ type phase. Pulse current sintering under a high applied stress made it possible to prepare dense Ti–38 at.%Zr–17 at.%Ni compacts having predominant icosahedral grains.

References

[1] W.J. Kim, P.C. Gibbons, K.F. Kelton, Philos. Mag. A 78 (1998) 1111–1124.
[2] A. Takasaki, C.H. Han, Y. Furuya, K.F. Kelton, Philos. Mag. Lett. 82 (2002) 353–361.
[3] A. Matsumoto, K. Kobayashi, T. Nishio, K. Ozaki, Abstracts of Eighth IUMRS International Conference on Advanced Materials, 2003, p. 225.
[4] A. Matsumoto, K. Kobayashi, T. Nishio, K. Ozaki, J. Metastable Nanocrystalline Mater. 24–25 (2005) 335–338.
[5] P.C. Gibbons, K.F. Kelton, in: Z.M. Standik (Ed.), Physical Properties of Quasicrystals, Springer, 1999, p. 403.
[6] K. Foster, R.G. Leisure, J.B. Shaklee, J.Y. Kim, K.F. Kelton, Phys. Rev. B 59 (1999) 11132–11135.
[7] J.B. Qiang, Y.M. Wang, D.H. Wang, M. Kramer, P. Yhiel, C. Dong, J. Non-Cryst. Solids 333 and 335 (2004) 223–227.
[8] A. Matsumoto, K. Kobayashi, T. Nishio, K. Ozaki, Mater. Trans. 43 (2002) 2039–2043.
[9] M.V. Nevitt, Trans. Met. Soc. AIME 218 (1960) 327.
[10] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Elsevier Science Publishers B.V., The Netherlands, 1988.
[11] K.F. Kelton, W.J. Kim, R.M. Stroud, Appl. Phys. Lett. 70 (1997) 3230–3232.
[12] S. Yi, K.B. Kim, W.T. Kim, D.H. Kim, Scripta Mater. 44 (2001) 1757–1760.