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On the formation of nano-sized quasicrystals in $Ti_{53}Zr_{27}Ni_{20}$ alloy

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Abstract

We report here the formation of a nano-quasicrystalline (qc) phase in the melt spun ribbons of $Ti_{53}Zr_{27}Ni_{20}$ alloy based on the results of transmission electron microscopy (TEM). Such a phase was formed by employing melt spinning of the alloy, at a wheel speed of 40 m/s. The nano-qc phase (30–40 nm) was detected through diffraction monitored by 30 nm electron probe using TEM. Together with this crystalline phases were found to coexist. These crystalline phases were found to be belonging to cubic crystal system ($a = 3.40$ Å) and a hexagonal phase ($a = 5.21$ Å, $c = 8.53$ Å). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Quasicrystals; Transmission electron microscopy; Alloy systems

1. Introduction

Quasicrystals are very interesting and comparatively new phase of solids. Since the discovery of quasicrystals in Al–Mn system [1], their occurrences have been confirmed in variety of alloy systems [2]. Most common qc systems are either aluminium (Al) or titanium (Ti) based. The known Ti-based systems are far less in number than Al-bearing qc materials owing to difficulties in their synthesis. However, they posses interesting characteristic. They have their potential promises with respect to formation of new structural variants and many unusual physical properties [3]. We believe that synthesis of nano-scale qc in Ti-based systems and their influence on properties will be important, in view of emphasis of nano-technology in future [4].

2. Experimental details

Alloy ingots of $Ti_{53}Zr_{27}Ni_{20}$ were prepared by RF-induction melting of a corresponding stoichiometric mixture of 99.9% pure Ti, Zr and Ni in purified graphite crucible under argon atmosphere. The alloy ingots were then subjected to rapid solidification employing melt spinning at various tangential speeds ranging from 25 to 50 m/s. After rapid solidification, 30–40 μm thick and 4–5 cm long ribbons were produced. The ribbons were then extensively investigated by transmission electron microscopy (Phillips-EM CM-12). For TEM studies, the ribbons were electropolished at -20°C using 5% $HClO_4$ in methanol as electrolyte.

3. Results and discussion

It has been observed that the sizes of grains in crystals vary during rapid quenching depending on certain parameters. Some of which cannot be controlled easily. However, it is possible to control wheel speed and pressure of jet. Hence, in the present investigation, we have utilized a range of speeds (25–50 m/s) and pressures of inert gas (50–100 atm) for knowing the possible formation of nano-quasicrystals. It was found that speed of wheel of about 40 m/s (above which totally amorphous phase were formed) and pressure of jet at 90 atm (above which the melt was sprayed in the form of droplets resulting in powder formation rather than ribbon) was optimum for the formation of ribbons with nano-quasicrystalline phase. The nominal composition of these ribbons was $Ti_{53}Zr_{27}Ni_{10}$. Special care was taken to avoid silicon (Si) contamination originating from reaction with silica tube employed during melt spinning. The alloy was melted quickly by suitably adjusting the RF power input.

The selected area diffraction patterns of the electropolished ribbons revealed the presence of both quasicrystalline and crystalline phases. Representative diffraction patterns each recorded from regions dominated by random orientations of quasicrystalline and crystalline grains respectively are shown in Figs. 1 and 2. Fig. 1 consists of rings, which becomes explicable based on a quasilattice constant (a_R)

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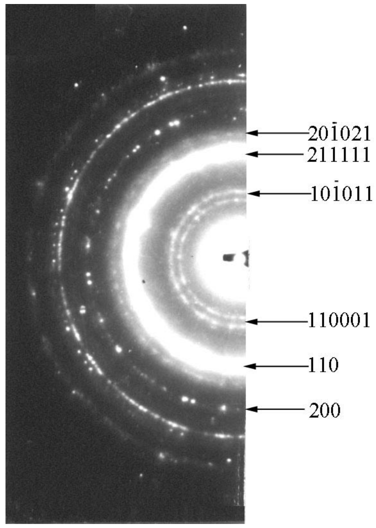

Fig. 1. Selected area diffraction patterns from the crystalline– quasicrystalline aggregates.

equal to 5.18 Å (this corresponds to known quasilattice constant of this alloy [5]). The sextuplets of indices of first few rings are also indicated. Some of the rings could be explained based on a cubic cell with lattice parameter of 3.40 Å. They however are very close to some of the reflection of IQC phase. Hence, this may require further delineation. The bright field image corresponding to this ring pattern is shown in Fig. 3. This indicates fine grains (nano-phase ∼40 nm) of quasicrystalline phase. The distinct microstructural characteristics, shown in Fig. 4, vis-à-vis that of Fig. 3 indicate independent nucleation and growth of the hexagonal phase. In order to confirm the formation of nano-quasicrystals, the CBED diffraction and dark field imaging from fine grain region of quasicrystalline phase were recorded. A representative CBED diffraction pattern is shown in Fig. 5 and the dark field image (by taking

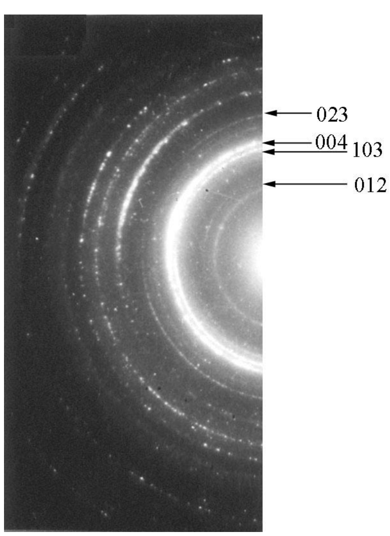

Fig. 2. Selected area diffraction patterns from hexagonal phase aggregates.

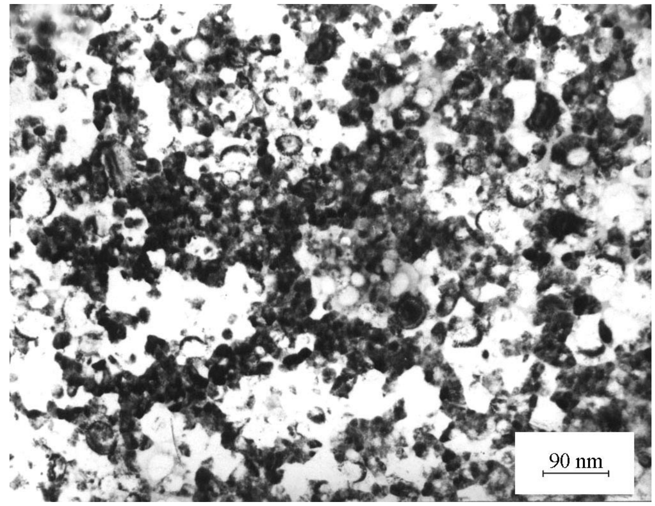

Fig. 3. Bright field image corresponding to SADP (Fig. 1) showing formation of nano-size quasicrystals and a cubic crystalline phase.

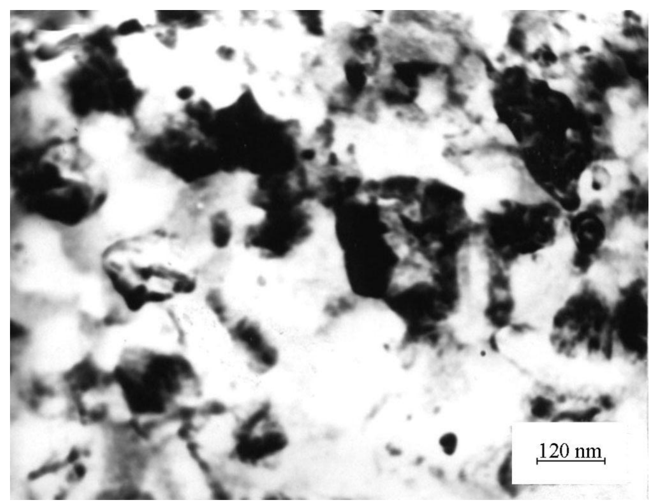

Fig. 4. Bright field image corresponding to SADP (Fig. 2) showing hexagonal phase formed due to different solidification condition.

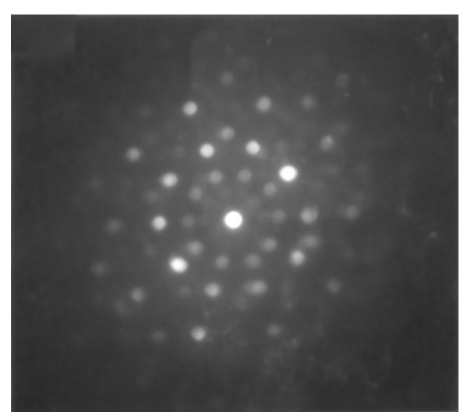

Fig. 5. CBED photograph showing fivefold symmetry taken from single nano-size grain of icosahedral phase.

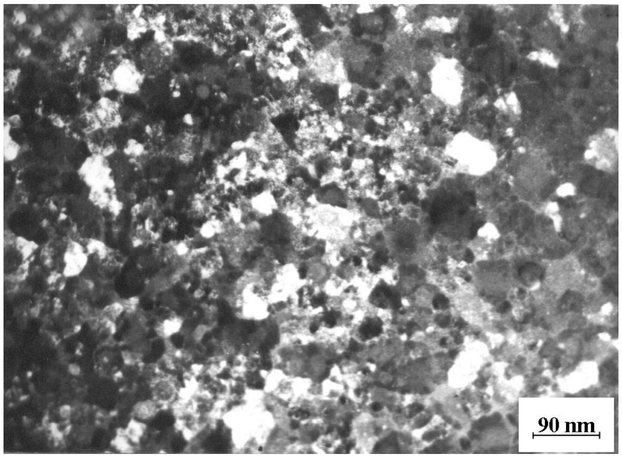

Fig. 6. Dark field image of region shown in Fig. 3.

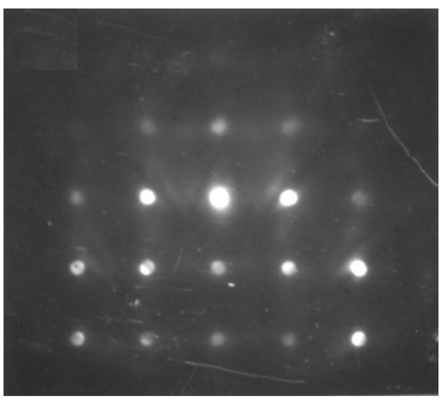

Fig. 7. CBED showing fourfold symmetry taken from single grain of b.c.c. phase.

2 1 1 1 1 1 ring of quasicrystal in the selected area aperture) is shown in Fig. 6. The occurrence of fivefold symmetry and the features in the dark field clearly confirms the presence of icosahedral phase. Studies spread on several $Ti_{53}Zr_{27}Ni_{20}$ alloy prepared with earlier described parameter confirmed the generality of the formation of nano-qc phase. The dark and distinct contrast on the periphery of rounded grains indicate coexistence of a crystalline phase which has been delineated further by conducting CBED with the help of nano-probe (30 nm). A representative pattern is shown in Fig. 7. The microstructure around the periphery may arise owing to sympathetic nucleation condition being available during rapid solidification. The diffraction rings shown in Fig. 2 get indexed based on the lattice parameters of the hexagonal phase ($a = 5.21$ Å and $c = 8.53$ Å) [3]. This may be due to the different cooling rates which the melt experiences during spinning. Moiré fringes are also seen in Fig. 4 in some of the faceted grains indicating juxtaposition of various crystalline grains.

To investigate any possible role of silicon contamination in stabilizing the nano-qc phase, the regions showing this phase were subjected to extensive EDAX explorations. The EDAX spectrum did not show the presence of Si. It can, therefore, be inferred that the formation of nano-qc phase is not triggered by Si contamination. The composition of this phase has been found to be 51–53 at.% of Ti; 19–21 at.% of Ni and 27–28 at.% of Zr.

4. Conclusions

We therefore, conclude that the nano-quasicrystalline phase has been formed in $Ti_{53}Zr_{27}Ni_{20}$ system under rapidly solidification condition corresponding to a cooling rate achievable at a wheel speed of ~40 m/s. The coexistence of IQC ($a_R = 5.18$ Å) and a cubic crystalline phase has been suggested to occur due to sympathetic nucleation. The hexagonal phase ($a = 5.21$ Å, $c = 8.53$ Å) may result due to the strong chemical fluctuations present owing to non-equilibrium solidification condition. Further studies on the formation and characterization of Ti–Zr–Ni phase, particularly in regard to the development of single nano-size qc phase are being carried out presently and will be reported later.

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