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Metastable orthorhombic phases at ambient pressure in mechanically milled pure Ti and Ti–Mg

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Nanocrystalline Ti and Ti–20 at.% Mg produced by mechanical milling were characterized using nanobeam diffraction. Metastable ω (hexagonal) and γ (orthorhombic) phases were observed in the pure Ti, while γ, a new orthorhombic ε phase and a face-centred cubic (fcc) phase were identified in the Ti–Mg. γ, found so far only at high pressures, was produced by a combination of high impact pressure and shear stress during milling. The forced dissolution of Mg caused the formation of the ε and fcc phases.

Keywords: Metastable phases; Mechanical alloying; Titanium alloys; Magnesium; Immiscible alloys

At ambient pressure, titanium exists in hexagonal close-packed (hcp, α) form below 883 °C and in body-centered cubic (bcc, β) form above. However, titanium can exist at room temperature in different structures at high pressures, including hexagonal (ω) [1–5] and orthorhombic (γ [4,5] and δ [5]). The transformation from α to ω starts at ∼5–10 GPa, ω to γ at ∼115–130 GPa, and γ to δ at ∼140 GPa. Upon decreasing pressure, δ reverts to γ at ∼134 GPa and then ω at ∼120 GPa [5]; ω persists at ambient pressure due to hysteresis [2]. The formation of ω is attributed to reduced volume and to electron transfer from *s* to *d* [2,4]. ω can also be obtained by heat treatment or plastic deformation [6,7]. The transformations from α to ω and then to bcc can be predicted by first-principles calculations [8] although no bcc-Ti has been observed even at 216 GPa [5]. In addition, fcc-structured Ti has been reported in thin films [9,10], milled particles [11,12] and deformed bulk material [13], and suggested by first-principles calculations [8,14].

However, the orthorhombic γ and δ phases have only been observed at high pressures. There have been no reports of them in materials processed by other methods. Nor are there any calculations predicting their existence at ambient conditions. We report here the observations of γ in a milled Ti powder and a newly named orthorhombic ε and an fcc phase in a milled Ti-Mg powder using nanobeam diffraction (NBD). This is the first time these orthorhombic phases have been found at ambient pressure. In particular, ε exists only with an appreciable amount of Mg (∼2 at.%), whereas γ is associated with very low Mg (<∼0.5 at.%) and fcc with high Mg (∼25 at.%).

Pure Ti and a Ti–20Mg (at.%) alloy were prepared by ball milling (QM-3SP4 planetary) of a pure Ti (∼99.5% purity, 45 μm) powder and a mixture of the pure Ti and a pure Mg (∼99.8% purity, 45 μm) powders, respectively. The vials and balls were stainless steel with a ball to powder ratio of 20:1. The milling was conducted at 400 rpm for up to 120 h in high-purity argon with 4 wt.% of stearic acid. X-ray diffraction (XRD) was performed using a Bruker D8 Advance diffractometer with Cu K_α. Scanning and transmission electron microscopy (SEM/TEM) characterization was done using an FEI Quanta 200 SEM and FEI Tecnai F20 TEM at 200 kV. TEM samples were prepared using Nova Nanolab 200 focussed ion beam (FIB) at 30 kV. Energy-dispersive X-ray spectroscopy (EDX) was performed in the transmission electron microscope to determine the local compositions. NBD avoids the difficulties inherent to conventional XRD [15] and selected-area electron diffraction (SAED) [16,17]. NBD was used here with a convergence semi-angle of 0.67 mrad and a parallel beam size of 2.2 nm.

Figure 1 displays XRD and SAED patterns from the milled Ti powder. The peaks for α and ω are identified in Figure 1a. The SAED rings confirm randomly oriented nanocrystals, as observed in a cryomilled Ti powder [18]. A large number of NBD patterns were indexed, confirming α and ω and revealing orthorhombic γ which had only been

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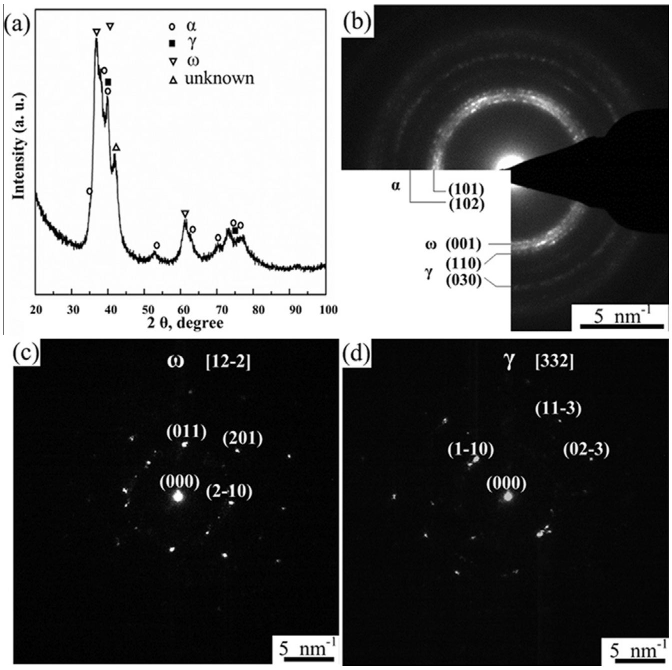

Figure 1. Ti powder milled for 40 h: (a) XRD and (b) SAED showing α, ω and γ and randomly oriented nanocrystals, and (c) and (d) NBD identifying ω and γ.

found previously under high pressure [4]. Figure 1c and d show NBD patterns indexed as ω and γ, respectively. Retrospectively, peaks and rings of γ can be found in Figure 1a and b. Some rings associated with α and ω can also now be indexed (Fig. 1b).

The results for the milled Ti–20Mg are shown in Figure 2. The α peaks are visible in Figure 2a although they are not as prominent as in Figure 1a. In addition, three peaks are attributed to an fcc structure with a lattice parameter of $a = 0.429$ nm, similar to that reported in some Ti–Mg compositions [19–21]. Figure 2b shows alternating Ti- and Mg-rich layers resulting from deformation, fracture and cohesion of particles [22], as revealed by EDX of the same area in Figure 2c. Many NBD patterns from the Ti-rich region were indexed to γ (Fig. 2d) or a new orthorhombic phase named ε (Fig. 2e). High-resolution (HR)TEM with fast Fourier transformation (FFT) from the framed area (Fig. 2f) and NBD (Fig. 2g) from the powder milled for 120 h confirmed the presence of ε. Again, peaks for γ and ε can be retrospectively identified in Figure 2a. The α and fcc phases are confirmed by NBD although the fcc phase is only found in areas with ~25 at.% Mg. The fcc phase is not one of TiC, TiO and TiN (all fcc-structured with $a = \sim 0.43$ nm [12]) since EDX showed very low concentrations of C, O and N, and moreover, if contamination during milling by C, O and N were to cause their formation, these compounds would have been observed in the milled pure Ti as well (which was not the case here).

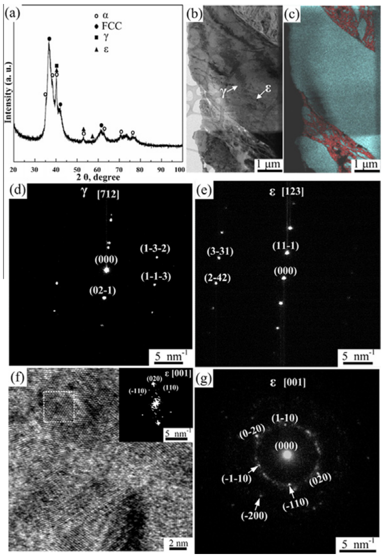

Figure 2. Ti–20Mg powder milled for 40 h: (a) XRD showing α, γ, ε and fcc; (b) TEM indicating locations of NBD in (d) and (e); (c) EDX of (b) showing Mg (red) and Ti (blue); (d) and (e) NBD identifying γ and ε; (f) HRTEM and FFT (inset) from the square, confirming ε; and (g) NBD from ε in the powder milled for 120 h.

The relevant phases are listed in Table 1. α belongs to $P6_3/mmc$ (194) with $a = 0.2950$ and $c = 0.4682$ nm. ω is hexagonal with three atoms in the unit cell at (0, 0, 0), (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2), and its lattice parameters are pressure dependent [4]: a decreased from 0.4600 to 0.3904 nm and c from 0.2820 to 0.2436 nm at 124 GPa [4,5]. It is well known that temperature [23], pressure [4], shock loading [24] and plastic deformation [6,7] can cause a martensitic transformation from α to ω [25]. Less known are some recent experiments showing that ω can transform into γ with increasing pressure [4]. γ is orthorhombic, belonging to $Cmcm$ (63); the unit cell has four atoms occupying the 4c Wyckoff positions (0, y, 1/4), (0, $-y$, 3/4), (1/2, $y + 1/2$, 1/4) and (1/2, $-y + 1/2$, 3/4) with $y = 0.11$ and $a = 0.2388$, $b = 0.4484$ and $c = 0.3915$ nm [4]. On further increasing pressure to ~140 GPa, γ transforms into δ which is orthorhombic and in the same space group but with different lattice parameters [5].