4th International Light Metals Technology Conference
Edited by M.S. Dargusch

Ti-Mg ALLOY POWDER SYNTHESIS VIA DIRECT REDUCTION OF TiO_2

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Abstract

This paper reports the preliminary results of an investigation on the synthesis of a Ti-Mg alloy powder through mechanochemical processing of TiO_2 and Mg powders. TiO_2 was mixed with elemental Mg according to a nominal stoichiometric composition with 15wt% excess Mg. The powder mixture was mechanically milled in a Simoloyer high energy ball mill for durations of 2, 4, 8, 16 and 24 hours. Contamination was minimised by processing under a high purity argon atmosphere.

Changes in phase compositions were studied using the XRD techniques. TiO_2 was reduced, as shown by the formation of MgO. The extent of the reduction, as indicated by XRD peaks' intensities, increased with milling time. The XRD spectra of powders milled for 24 hours revealed virtual disappearance of TiO_2 peaks and there was no evidence of elemental Ti. The lattice parameter of the resultant alloy powder was larger than that of elemental Ti. This implies that the Ti was alloyed with free Mg to produce Ti-Mg alloy powder. The lattice parameter increased with increasing milling time.

Introduction

Titanium (Ti) is the fourth most abundant structural metal in the earth's crust. However, its widespread use is hampered by the high cost of production using the current commercial Ti production process (the Kroll Process). The process is labour and capital intensive [1]**.** Research work is being conducted on direct reduction of rutile by more reactive metal reductants. Direct reduction would avoid the many steps present in the Kroll Process; hence is potentially cheaper, and can also result in the formation of Ti alloys [2].

The alloying of Ti with magnesium (Mg) results in significantly lighter alloys, without compromising the mechanical properties [3]. Such light weight Ti alloys are particularly beneficial to the aerospace industry, where weight saving is a priority. Currently, there are no commercial Ti-Mg alloys with high content of Mg. This is due to the low solid solubility of Mg in Ti under equilibrium conditions [3]. Mechanochemical Processing (MCP) has the potential to produce Ti-Mg alloys with high Mg-content. MCP is a process for preparing metal powders (and metal alloy powders) by the ambient temperature reduction of a reducible metal compound by a reactive metal or metal hydride [4].

Experimental Procedures

Sctoichiometric quantities of commercially pure TiO_2 and Mg powders with 15wt% excess Mg were thoroughly mixed to produce a TiO_2-Mg blend. Starting powder particle sizes were: Mg - <150 μm and TiO2 - < 25 μm. The powder blend was milled for uninterrupted durations of 2, 4, 8, 16 and 24 hours respectively, using a Simoloyer CM01-2L high energy ball mill. The milling speed was 800 rpm and the ball to powder ratio (BPR) was 20:1. Hardened steel balls, of diameter 5 mm, were used as the milling media. A process control agent was added to the powder mixture to avoid excessive cold welding of the powders during milling. After milling, the powders were analysed by XRD using a Philips PW1710 diffractometer, with

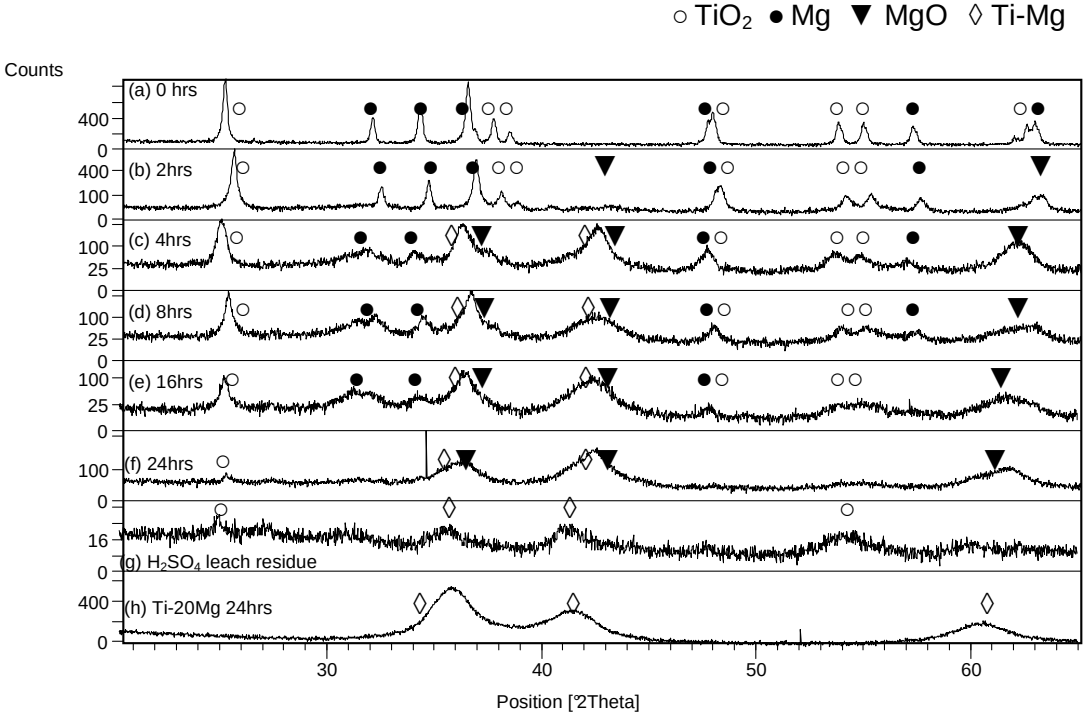
CuK∝ wavelength of 0.15483 nm. Powder morphology was investigated using a Jeol JSM-7 500F scanning electron microscope (SEM). Magnesium oxide (MgO) was leached out from the milled powders in a platform shaker at 200 rpm and 75°C using inorganic acid solutions. The resultant residue was rinsed with distilled water and dried in a vacuum before XRD analysis.

Results

X-ray diffraction

The XRD spectra of the TiO_2-Mg powder blend (a), the milled powder mixtures for the different durations (b-f), leach residue (g) and milled elemental Ti-Mg alloy powder (h) are shown in Fig 1. The peak intensities of TiO_2 and Mg peaks gradually decreased and broadened with increasing milling time. The peak broadening effect indicates reduction in the grain sizes. A new peak, identified as that of MgO could already be seen after milling for 2hrs (Fig. 1 (b)), signifying that the reduction reaction was already activated. The Mg peak at 2θ 37° shifts to lower 2θ values after milling for 2hrs; this may have been due to that the Ti that is initially formed from the reduction reaction got dissolved into Mg. Milling beyond 2 hours did not produce any new peaks but served to move forward the reduction reaction. For example, only very small TiO_2 peaks remained after milling for 24 hours, while the peak at 2θ 42.5° kept increasing in intensity. Also, peaks broadened, indicating that phases were becoming nanocrystalline or amorphous. The XRD pattern of TiO_2-Mg mixture milled for 24hrs (Fig 1(f)) resembled that of elemental powders (Fig. 1(h)) implying the phases in milled TiO-Mg mixture were similar to those in the milled Ti-Mg mixture. The peaks at $2\theta \sim 36.5°$, 42.5° and 62.0° on the XRD spectra of the milled elemental powders belong to fcc Ti-Mg solid solution [8].

Fig 1: XRD spectra of the TiO_2-Mg powder mixture milled at 800 rpm for various durations and along with that of elemental Ti-20Mg powders.

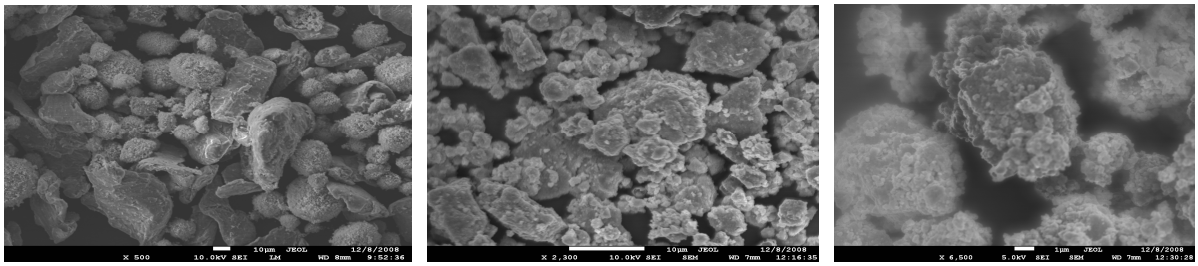


Morphological evolution

Figure 2 gives the morphologies of the milled TiO_2-Mg powders, as a function of milling time. The irregular platy particles in Fig. 2 (a) were identified by EDX, as Mg metal powder while the perfectly spherical particles were TiO_2 powder. There was a discernable size difference between the Mg and TiO_2 powders, with the former being coarser.

Fig 2: SEM micrographs of TiO_2-Mg powders milled for different durations.

(a) As blended **(b) 8 hours** **(c) 24 hours**



The Mg powder particles lost their initial morphologies which were replaced by a globular morphology while the TiO_2 powder particles were indistinguishable as early as after milling for 2hrs. It is possible that the TiO_2 particles, which are expected to be brittle, already fractured and were lodging themselves into the soft Mg particles. Higher magnifications revealed that the globular particles themselves were agglomerates of smaller particles welded together. This evolution of morphology is in line with the ball milling process which proceeds through repeated welding, fracturing and rewelding of powder particles, [5]. The sizes of the Mg powder particles decreased from 100 microns to values lower than 100 nanometres after 24 hours of milling. The degree of homogeneity appeared to increase with milling time.

Leaching out of magnesium oxide

The Rietveld refined peaks showing the presence of Ti-Mg alloy at $2\theta \sim 36.5°$, 42.5° and 62.0° coincided with the measured peaks for MgO. The milled powder was immersed in 0.3M hydrochloric acid (and also in 0.5M sulphuric acid) to leach out MgO [6]. XRD analysis of the residues (Fig. 1(g)) showed that the peak at $2\theta \sim 62°$ virtually disappeared from the patterns; indicating that it was an MgO peak. The other peaks at $2\theta \sim 36.5°$ and 42.5° lowered in intensity, showing presence of Ti-Mg alloy on those peaks after the MgO had been leached out.

Discussion

The observation of the formation of MgO (and the lowering in peak intensity of TiO_2 and Mg (Fig. 1) with increasing milling time on the XRD patterns suggests a typical oxidation-reduction reaction that involves displacement of Ti from TiO_2 by Mg, resulting in formation of MgO as indicated by Eq. (1)

$$TiO_2 + 2Mg = Ti + 2MgO \quad (1)$$

The enthalpy of formation for the formation of 2MgO is -1 204kJ which is about four times lower than that of TiO_2 (-315kJ), so that the reaction as mentioned in Eq. 1 is a forward single step reaction. The extent of the reduction of TiO_2 was evaluated using Equation 2:

$$D = \left(\frac{I(TiO_2)}{[I(TiO_2) + I(MgO)}\right) \times 100 \quad [7] \quad (2)$$

where I is the intensity of the diffraction peaks of Mg and TiO_2. The initial TiO_2 peak intensity was 1 625 while the final MgO peak intensity was 250. Therefore, the reduction of TiO_2 during milling was calculated to be 87%. It is the free Ti from Eq. 1 which, during further mechano-chemical processing, interacts with excess elemental Mg to form the Ti-Mg alloy. The peak at 36.5° formed early and is probably MgO from the initial redox reaction in equation (1). Using the Rietveld refinement analysis technique it was established that there was Ti-Mg phase. The XRD peaks for this phase coincide with those of MgO. However, when the MgO was leached out from the milled powder, the peak at $2\theta \sim 62.0°$ disappeared, showing that it represented the MgO phase only. The other peaks at $2\theta \sim 36.5°$ and 42.5° reduced in intensity indicating that the peaks were now representing the Ti-Mg phase only. These peaks appear in the same positions as those of Ti-20%Mg (Fig. 1(h)) synthesised from elemental Ti and Mg, from an independent project at the CSIR [8].

The peak broadening effect (Fig. 1(b-f)) indicates that the milling process resulted in nanocrystalline grains in the product phases (Ti-Mg and MgO). In addition, the lattice parameter increased significantly to 0.424 nm at 24 hours; pure Ti has a lattice parameter of 0.295 nm. The expanding lattice structure resulted from mechanical milling and dissolution of Mg in Ti.

Conclusions

The milling of TiO_2 and Mg was able to reduce TiO_2 to Ti and form a Ti-Mg alloy powder and MgO as shown by the formation of three new peaks at $2\theta \sim 36.5°$, 42.5° and 62.0°.Preliminary leaching experiments appear to show that MgO can be leached out from the new powder mixture but more work will be carried out to ascertain this.

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