



Effect of pressure on the metastable phase formation of equilibrium immiscible Ti-Mg system studied by *ab initio* technique and mechanical milling

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INTRODUCTION

Titanium (Ti) and its alloys are very important materials from both technological and scientific point of view. These class of materials received attention due to their interesting properties such as lightweight, strength and stiffness, as well as corrosion resistance. Since reducing density is the most effective way of lowering the overall weight of a structural component [1], which in turn leads to a decrease in energy consumption, it would be ideal to alloy Ti with other lighter metal elements such as magnesium (Mg) and aluminium (Al). This is because Mg has a low density of 1740 kg/m³ which is approximately 35% lighter than Al alloys and 65% lighter than Ti (1941K). Unfortunately, Ti and Mg do not mix under normal equilibrium conditions using conventional melting techniques. This is due to the large difference in temperature, i.e., Mg boiling point is 1380K, much lower than melting point of Ti (1941K). Therefore, the only possible route so far to achieve alloying of Ti and Mg, is by employing a non-equilibrium process. As a result, many attempts to extend the solid solubility have been made in the past decade using non-equilibrium processes [4], e.g. ion-beam mixing (IBM) [5], mechanical milling (MM) [6], solid-state-reaction (SSR) [7] and high-pressure-anvil-cells (HPAC) [8].

Among them, MM is economically viable and also produces new materials (amorphous and nano-structured) with unique and enhanced properties, in some cases even synthesise alloys between elements that are immiscible in nature in solid-state [9]. Until now, only up to 24 at.%Mg could be dissolved in Ti by MM [10]. It was recently reported that up to 50 at.%Mg is soluble by MM [11,12], although, it is not known to what extent solid solubility is possible and which crystal structures form in the Ti-Mg system.

High Pressure is known to influence electronic structure and crystal packing and in some cases induce compound formation between immiscible elements [13]. Therefore, the study of pressure induced formation is intended.

METHODOLOGY I: AB INITIO CALCULATIONS

Our *ab initio* calculations were performed using the well-established total energy code, CASTEP[10], which is based on quantum mechanics for performing electronic structure calculations. The maximum plane wave cut-off energy of 400 eV was employed on alloys, using Vanderbilt-type ultrasoft pseudopotentials (US) [14] to describe the electron-ion interaction. The integration in the Brillouin zone (BZ) is done on the special k-points determined from the Monkhorst-Pack scheme [16]. The energy cut-off, as well, as the number of k-points were converged to within 1 meV per atom. Hydrostatic pressure, of up to 250 GPa, was applied on the promising optimised structures showing the lowest heat of formation to investigate if high pressure can induce the formation of Ti-Mg alloy. The *ab initio* calculations were performed to predict the possible metastable phases of A3B, AB and AB3 type in the Ti-Mg system, which has no alloy phase over the entire composition range.

RESULTS

Table 1: Structural and cohesive properties of Ti₃Mg and TiMg₃ phases

Phase	a (Å)	c/a
Ti ₃ Mg		
A15	5.26	
DO ₁₈	4.60	1.82
DO ₁₉	5.92	0.80
DO ₂₂	4.12	2.06
DO ₂₃	4.15	4.04
DO ₃	6.61	
L1 ₂	4.16 (4.25) ^[7]	
TiMg ₃		
A15	5.55	
DO ₁₈	4.94	1.78
DO ₁₉	6.20	0.79
DO ₂₂	4.90	1.41
DO ₂₃	4.45	3.82
DO ₃	6.91	
L1 ₂	4.35	
	(4.40) ^[7]	

Table 2: Structural and cohesive properties of TiMg phases

Phase	a (Å)	c/a
TiMg		
B18	4.97	2.41
B2	3.36 (3.445) ^[9]	
B32	6.11	
B _h	2.91	1.80
	(3.03) ^[9]	(1.60) ^[9]
	(3.03) ^[9]	(1.67) ^[9]
L1 ₀	4.76	0.70

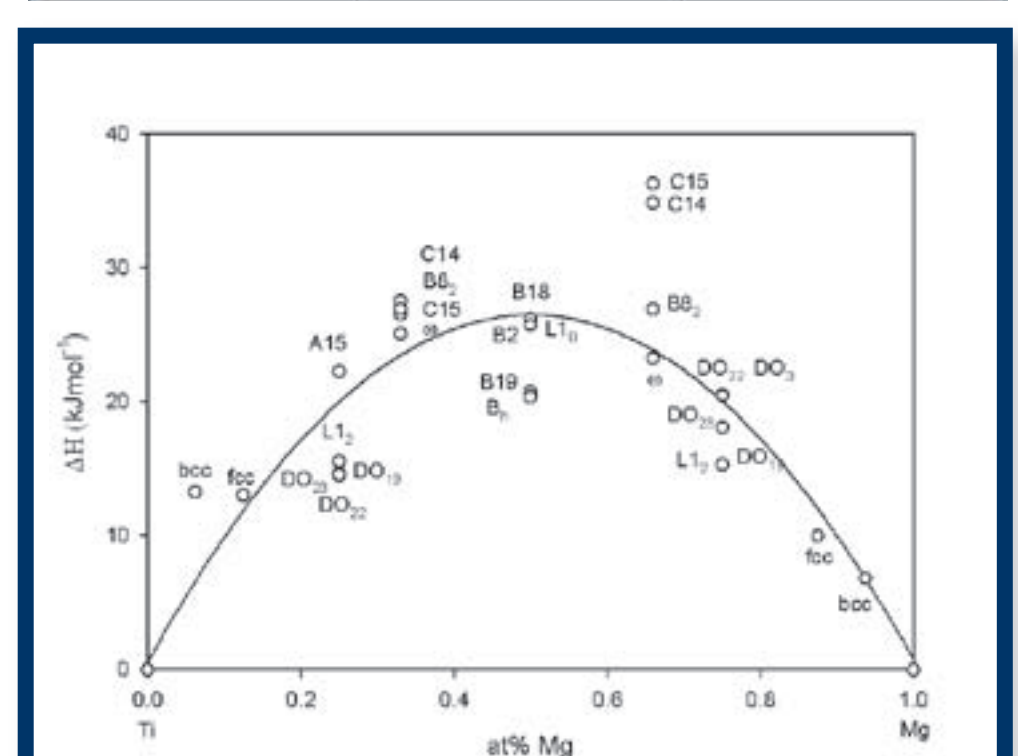


Figure 1: Predicted heats of formation as a function of Mg atomic composition

CONCLUSION I

- The hypothetical crystalline structures of Ti-Mg system were successfully calculated by first principles method.
- We used static-lattice enthalpies to deduce the phase stabilities of Ti-Mg alloys under pressure.
- At low pressure the heat of formation for Ti-Mg is large and positive in accordance with very little solubility of Mg in Ti.
- Hence, first principles calculations could also be used to predict possible crystal structures of compounds or phases that could be formed from thermodynamically immiscible elemental metals.
- The predicted hypothetical crystalline structures of the Ti-Mg system, has positive heat of formations, confirming the immiscibility of the two metals

(Ti and Mg) in each other at equilibrium, and are in agreement with experiments [17].

- Thus, pressure tends to induce the ability of elements to form alloys, probably due to Ti phase transition from hcp to fcc lattice around 100 GPa, the pressure at which this tendency towards alloying is observed. This means that already at zero temperature there is a transition from the tendency towards phase separation between Ti and Mg at low pressure to the tendency towards alloying at higher pressure. It is interesting to note that above 80 GPa, the lattice parameter c of Ti suddenly increases with pressure while lattice parameter a decreases faster. It is therefore anticipated that, using far-from-equilibrium processing techniques that are capable of providing adequate energy, metastable Ti-Mg phases predicted by *ab initio* calculations may be formed.

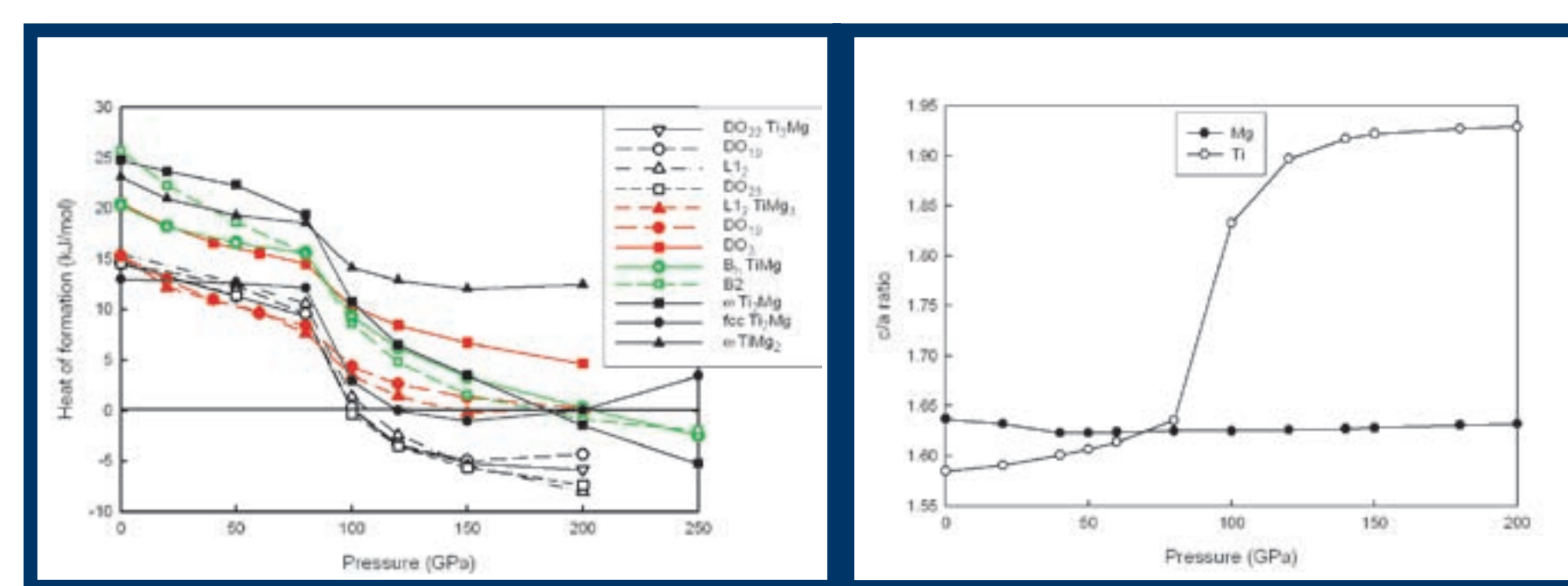


Figure 2: Heats of formation for various phases as a function of pressure

Figure 3: c/a ratio of hcp Ti and Mg as a function of pressure

METHODOLOGY II: EXPERIMENTAL PROCEDURE

Mechanical Milling

The starting material is high-purity Ti and Mg powders. Mixture of 50 at.% Ti and 50 at.% Mg (66.2 wt.% Ti) powder with powder to ball ratio of 1:20 was used. Powder charge amount was 100 g. Samples were prepared in a high energy ball mill (Zoz Simoloyer) using a 2l stainless steel vial and stainless steel balls. Samples were milled in Ar atmosphere. Stearic acid was used as PCA. The rotational speed of 800 rpm was employed for milling times of up to 72 hours.

Characterisation

Phases and microstructures were examined using a Philips PW 1830 diffractometer with a monochromatic CuK radiation ($\lambda=0.15405$ nm). Microstructural features of the powder particles were studied using a LEO 1525 FE-SEM with Oxford Link Pentafet EDS detector, operating at 10 kV.

RESULTS: EXPERIMENTAL & SIMULATED XRD PATTERNS

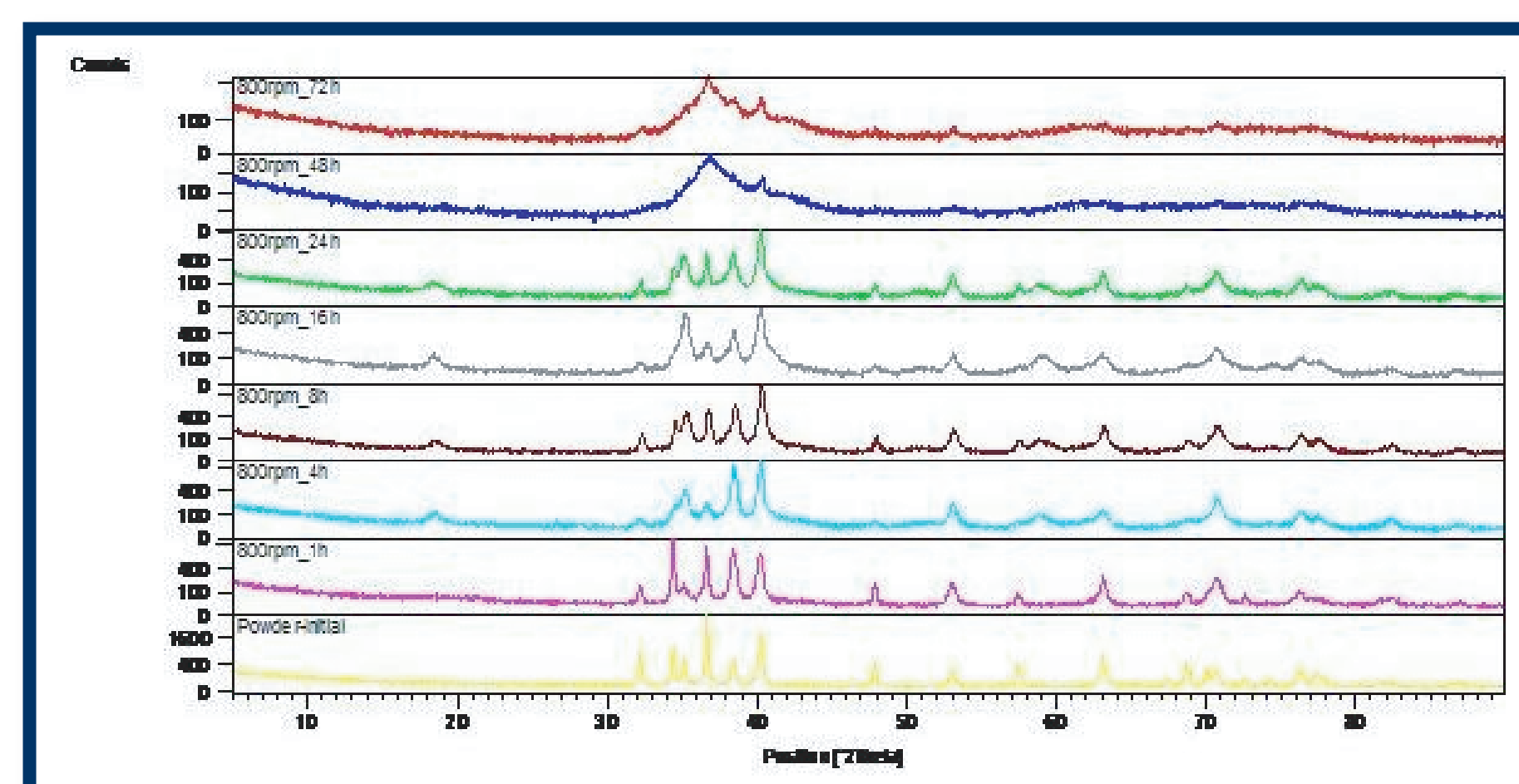


Figure 4: XRD patterns at various milling times

SEM IMAGES AT VARIOUS MILLING TIMES

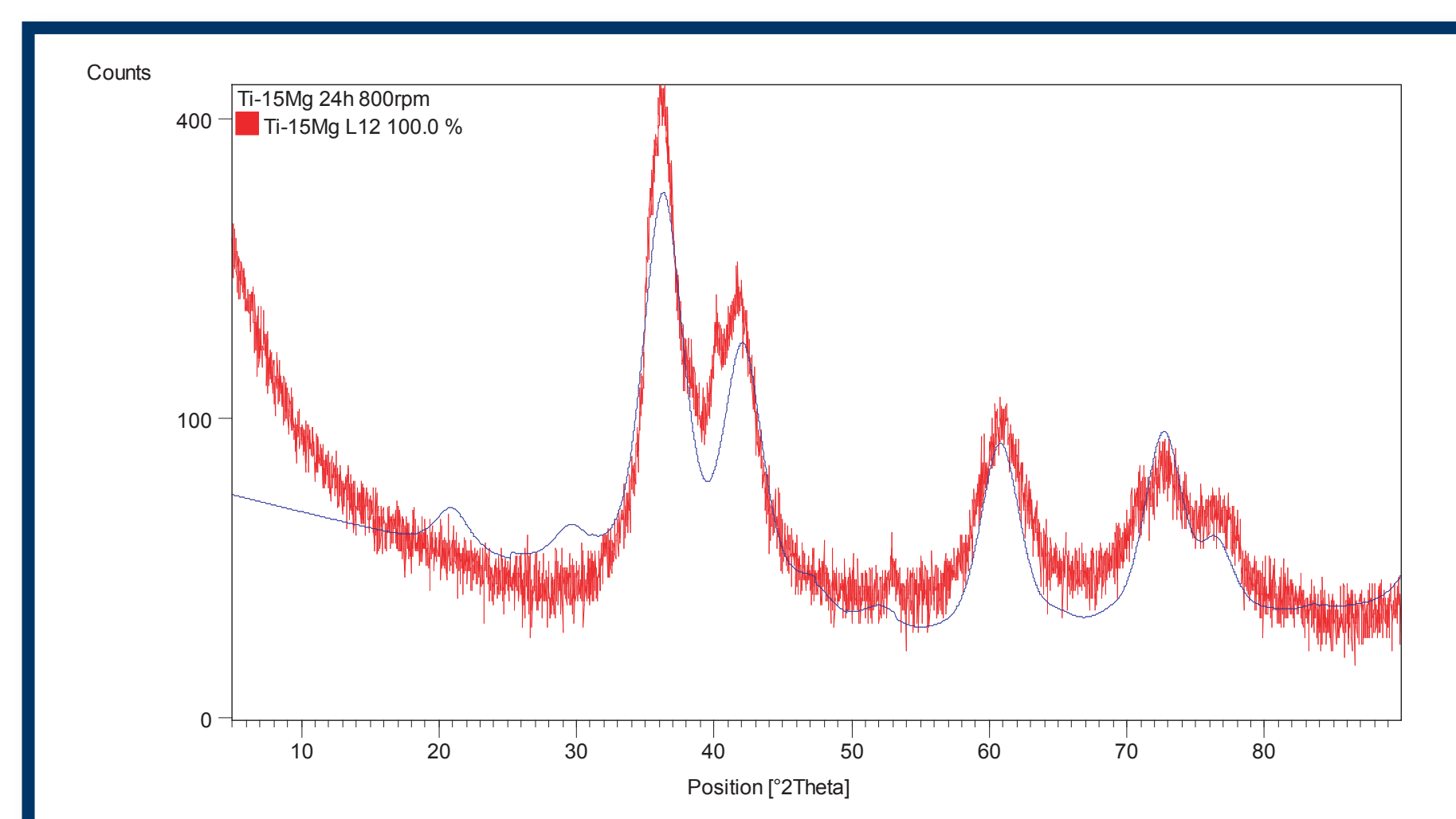


Figure 5: XRD pattern fitted with Rietveld analysis using High Expect Score Plus

CONCLUSION II

- The extended solid solubility of the initial 50-50 at.% Ti-Mg by means of high-energy ball milling was demonstrated by the SEM and XRD analyses.
- A single metastable hexagonal phase was formed after 48h ball milling at 800 rpm, under 2 bars Ar, in a Simoloyer (Zoz made).
- The EDX analysis revealed the chemical composition of the single phase being Ti56Mg44 to Ti51Mg49, which is very close to the initial equimolar composition of the powder mixtures and the targeted Ti50Mg50.

Since reducing density is the most effective way to lower the weight of a structural component, the CSIR is exploring options of mixing titanium with lighter metal elements such as magnesium and aluminium to help decrease energy consumption.



- The formation of an unstable fcc phase was observed at an intermediate milling time of between 4 and 24h. The reflection peaks of the fcc phase disappeared after a longer milling time, when the metastable hexagonal phase became the only constituent of the system.
- The intermediate unstable fcc phase coexisted within the plastically deformed heterogeneous layered Ti-Mg particles, and could not be seen under the SEM.

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