

Journal of Alloys and Compounds 297 (2000) 246-252



www.elsevier.com/locate/jallcom

Synthesis of a low-density Ti-Mg-Si alloy

O.N. Senkov*, M. Cavusoglu, F.H. (Sam) Froes

Institute for Materials and Advanced Processes (IMAP), College of Mines and Earth Resources, University of Idaho, Moscow, ID 83844-3026, USA

Received 1 June 1999; received in revised form 31 August 1999; accepted 31 August 1999

Abstract

A low-density titanium alloy was synthesized from blended elemental powders of TiH₂, Mg, and Si by mechanical alloying and/or heat treatment. The titanium hydride was used in place of titanium. Phase transformations occurring in the system during heating at a constant rate were studied with the use of DTA and XRD. During heating of the blended elemental powders decomposition of titanium hydride occurred in the temperature range 550–750°C and some silicon went into solid solution in titanium while the majority of the silicon reacted exothermically with magnesium at about 500°C producing an intermetallic phase Mg₂Si. This phase was stable on heating up to 950°C, where a eutectic component of this phase began to melt leading to formation of a liquid solution of magnesium in silicon, followed by a reaction of the liquid silicon with titanium and formation of a Ti₅Si₃ phase. A third reaction in the system was detected at about 1100°C due to formation of MgO, so that after annealing at 1150°C three stable phases, Ti(Si), Ti₅Si₃, and MgO, were present in the alloy. No decomposition of the Ti₅Si₃ phase or formation of Mg₂Si were detected either during subsequent cooling or a second heating of the alloy. Completely different kinetics of the phase reactions occurred in the mechanically alloyed powders. Magnesium and silicon dissolved in the titanium hydride during mechanical alloying. Decomposition of the titanium hydride occurred at 320–600°C, the Mg₂Si phase was formed after heating to 450°C, and the Ti₅Si₃ phase was detected after heating to 570°C. The Mg₂Si decomposed completely at a temperature of 650°C with the formation of MgO and Ti₅Si₃. After heating to 1150°C, three stable phases, TiN_{0.3}, Ti₅Si₃, and MgO, were present in the alloy. A discussion of the results is given. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Low density Ti-Mg-Si alloy; Synthesis; Mechanical alloying; X-ray diffraction

1. Introduction

Titanium alloys offer attractive combinations of high strength and toughness, corrosion resistance and elevated temperature properties. In recent years, improvements in the characteristics of these materials have come mainly from improved synthesis or processing methods rather than from the more traditional approach of improved understanding of chemistry-microstructure-mechanical property relationships. The goal is to move to an enhanced trend band, when parameters such as strength, stiffness, and temperature capability are improved, while other characteristics such as fracture toughness, fatigue crack growth rate and cost also have acceptable values [1]. One of the most important characteristics of titanium alloys is high specific strength, which is a result of high strength and low density of the alloys. It has been found that the density reduction is three to five times more effective in reducing the structural weight of parts than increasing strength and modulus [2]. Additions of low-density alloying elements such as magnesium, silicon and aluminum reduce the density of titanium.

The alloying behavior of the light elements with titanium varies widely depending on their physical and chemical properties (Table 1). The atomic size and electronegativity of aluminum are close to those of titanium, and this results in the solubility of aluminum in titanium being about 11 at.% at room temperature, a value which increases continuously with temperature. At sufficiently high aluminum levels, the ordered phases α_2 (Ti₃Al) and γ (TiAl) are formed. Silicon differs widely from titanium in atomic size and electronegativity. Because of this, it shows a limited solid solubility and forms intermediate phases with titanium such as Ti₃Si and Ti₅Si₃ [3]. Aluminum and silicon have already been alloyed with titanium to the highest possible levels of solubility, and intermetallic Ti-Al-Si alloys and composites have recently been developed [4-6].

Magnesium exhibits a big difference in atomic size and electronegativity compared to titanium [7]. Under equilibrium conditions magnesium is immiscible with titanium in the solid state. Moreover, the boiling temperature of

^{*}Corresponding author.

Table 1 Properties of magnesium, aluminum, silicon, and titanium [7]

Element	Atomic size (Å)	Electro- negativity	Density (gm/cc)	Melting point (°C)	Boiling point (°C)	Maximum solubility in α-Ti (at.%)	Maximum solubility in β-Ti (at.%)
Mg	1.72	1.31	1.74	650	1090	1	11
Al	1.82	1.61	2.70	660	2520	52	47
Si Ti	1.46 2.00	1.90 1.54	2.33 4.51	1410 1670	3260 3300	<0.5	5

magnesium is below the melting temperature of titanium, so that the elements cannot be alloyed by a conventional method. Non-equilibrium processing techniques such as vapor deposition and mechanical alloying can, however, be effective methods for Ti–Mg alloy design. For example, the solubility of magnesium in titanium can be considerably extended with these methods [8–11]. Magnesium is a promising alloying element for titanium density reduction. It was estimated [8] that each 1 at.% of magnesium in solid solution leads to about 1% density reduction. However, the two-component Ti–Mg solid solution is unstable and during heating it decomposes into titanium and magnesium. Silicon added to this system may react with both magnesium and titanium producing fine reinforcing particles of Ti_5Si_3 or Mg_2Si .

In the present work, a Ti-Mg-Si system was chosen for study. The goal of the work was to study phases and phase transformations in the Ti-Mg-Si alloy produced either by mixing elemental powders or by mechanical alloying elemental powders.

2. Experimental procedures

Powders of a titanium hydride, magnesium, and silicon were used as starting materials. The powders were mixed in the proportions of 80 wt% TiH₂, 12 wt% Mg and 8 wt% Si, and part of the mixture was mechanically alloyed in a SPEX-8000 high energy ball mill for 8 h in an argon atmosphere. The grinding media was hardened 4.8 mm diameter balls of 52100 steel, with a ball-to-powder ratio of 10:1. During milling the vial was cooled with a fan in order to minimize the temperature increase of the powders. Titanium hydride was used instead of titanium in order to accelerate the mechanical alloying process and reduce contamination [12]. Hydrogen can be easily removed from titanium products by vacuum annealing [13].

Differential thermal analysis (DTA) of both blended and mechanically alloyed powder mixtures was performed on heating in the range of 100 to 1150°C in an argon atmosphere using DTA-7 Perkin Elmer equipment, with a heating rate of 20°C per minute. After reaching a temperature the powder was immediately cooled down with a heating rate of 20°C per minute. The phases present in the powders were examined with the use of a Siemens 5000 X-ray diffractometer.

3. Results

3.1. As-blended powders

Fig. 1 shows a DTA curve for the as-blended powder with several exothermic and endothermic peaks, associated with phase reactions. The first exothermic peak has an onset at 483°C and maximum at 509°C. This is followed by a wide endothermic peak with an onset at 563°C and minimum at 638°C. The second exothermic peak has an onset at 940°C and maximum at 960°C and is preceded by a small endothermic peak. The third exothermic reaction, also preceded by an endothermic reaction, is detected near 1100°C. To understand the origin of these reactions, the powder was heated to a specific temperature (i.e. 540, 630, 875, 990 and 1150°C, see Fig. 1) and immediately cooled after reaching this temperature, and the phases present were analyzed with the use of XRD (Fig. 2).

Three phases, titanium hydride, magnesium and silicon, were present in the as-blended powder mixture (Fig. 2a). The intensity of the XRD peaks from magnesium and silicon decreased to almost zero and new XRD peaks corresponding to the Mg₂Si phase appeared after heating to 540°C (Fig. 2b), i.e. just above the first exothermic peak in Fig. 1. Essentially only two phases, α -Ti and Mg₂Si, were present after heating to 630°C, although traces of titanium hydride and silicon were also detected (Fig. 2c). After annealing at 875°C two major phases, Ti and Mg₂Si, and traces of Si were present in the system (Fig. 2d). After annealing at 990°C (Fig. 2e), Ti and Mg₂Si as major phases and Ti₅Si₃ and MgO as minor phases were detected, while only three phases, Ti, Ti₅Si₃, and MgO, were detected after annealing at 1150°C (Fig. 2f). No other



Fig. 1. DTA curve of as-blended powder.



Fig. 2. XRD patterns of blended elemental powder (a) as-blended and annealed at (b) 540°C, (c) 630°C, (d) 875°C, (e) 990°C and (f) 1150°C.

phase reactions occurred during subsequent cooling or further heating of the powders.

3.2. Mechanically alloyed powders

Fig. 3 shows the DTA curve of the mechanically alloyed powders. This DTA curve differs considerably from that for the as-blended powders (Fig. 1), indicating that the mechanical alloying affects the phase reactions in the powders. To understand the nature of these reactions, small amounts of the mechanically alloyed powder were heated in the DTA to various temperatures (350, 450, 600, 660, 900, and 1100°C) corresponding to specific points on the



Fig. 3. DTA curve of mechanically alloyed powder.

DTA curve (Fig. 3). After reaching a specific temperature, the powder was cooled to room temperature and analyzed using XRD (Fig. 4).

Compared to the as-blended powders (Fig. 4a), the XRD peaks from magnesium disappeared, the peaks from silicon became very weak, and the peaks from titanium hydride became wider and less intensive in the as-produced MA powder (Fig. 4b). Therefore, only two phases, the titanium hydride and traces of silicon, were detected. This may indicate that, during mechanical alloying, magnesium and silicon went into solid solution in titanium hydride and grain refinement of the titanium hydride occurred. The titanium hydride and silicon remained the only phases detected after annealing at 350°C (Fig. 4c), however after annealing at 450°C, a new phase, Mg₂Si, was detected together with TiH_{1.924}, while the XRD peaks corresponding to silicon completely disappeared (Fig. 4d). After annealing at 600°C the solid solution of Mg in the titanium hydride and titanium hydride itself decomposed and four phases, Mg, Mg₂Si, Ti₅Si₃ and Ti, were present (Fig. 4e). The magnesium peaks were very wide, indicating a very fine size of the magnesium precipitates. After heating at 660°C the peaks from magnesium and magnesium silicide disappeared, the intensity of the titanium silicide peaks increased and new peaks corresponding to MgO and TiN_{0.3} appeared in the XRD pattern (Fig. 4f). These three phases,



Fig. 4. XRD patterns of (a) as-blended, (b) as-mechanically alloyed (MA) and (c)–(h) MA and annealed powder mixtures. Annealing temperatures: (c) 350° C, (d) 450° C, (e) 600° C, (f) 660° C, (g) 900° C, and (h) 1150° C.

i.e. $TiN_{0.3}$, Ti_5Si_3 and MgO, were also detected after annealing at 900 and 1100°C, although their volume fractions, as determined by the relative intensities of the XRD peaks, changed.

4. Discussion

4.1. Phase reactions in as-blended powders

The analysis of X-ray diffraction patterns obtained from the powder samples heated to temperatures corresponding to characteristic points on the DTA diagram (Figs. 1 and 2) suggests that the first exothermic peak (near 500°C) is due to the reaction of magnesium with silicon and formation of magnesium silicide (Mg₂Si). This reaction occurs in the solid state, far below the melting temperature of magnesium (650°C). A wide endothermic peak in the temperature range 550 to 750°C appears to be associated with decomposition of the titanium hydride, hydrogen degassing and formation of free titanium, similar to observations in other work [6,14]. The results also indicate that the titanium does not react with silicon on heating to a temperature as high as 950°C, although some free silicon is present in the system, indicating that silicon has a higher affinity for magnesium than for titanium at the lower temperatures. However, decomposition of Mg₂Si and formation of Ti₅Si₃ do occur at higher temperatures (see Fig. 2). The reason for the decomposition of the Mg₂Si phase and formation of the Ti₅Si₃ at temperatures above 950°C can be rationalized by consideration of the binary Mg-Si phase diagram (Fig. 5). Because no reaction of titanium with silicon or magnesium was detected at temperatures below 950°C, the concentrations of silicon and magnesium in the as-mixed powders correspond to 60 wt% Mg-40 wt% Si composition in the binary Mg-Si system. This composition is marked by a vertical dashed line in Fig. 5 and corresponds to a hypo-eutectic composition (~92% Mg₂Si and 8% Si) with the eutectic isotherm at 945.6°C. It is evident that heating the sample above this temperature will lead to melting of the Mg₂Si-Si eutectic (this reaction is associated with a small endothermic peak, Fig. 1) and formation of a liquid silicon-magnesium solution. The subsequent exothermic



Fig. 5. Mg-Si phase diagram [17].

peak (near 960°C, see Fig. 1) may therefore be a result of reaction of the liquid silicon with titanium and magnesium oxidation (the oxygen is present in an argon atmosphere) producing the Ti₅Si₃ and MgO phases. According to the binary phase diagram, the endothermic and exothermic peaks near 1100°C can be explained by melting of the Mg₂Si phase with subsequent formation of Ti₅Si₃ and MgO. Ti, Ti₅Si₃ and MgO are the only species present in the system after heating to 1150°C. Because all the magnesium oxidizes, no back reaction occurs during further cooling and second heating of the powder. A further experiment should be performed in an oxygen-free atmosphere in order to determine if the Ti₅Si₃ is a stable phase in the Ti-Mg-Si system in the temperature range 20 to 1100°C or decomposes during cooling with formation of the Mg₂Si phase.

4.2. Phase reactions in mechanically alloyed powders

Mechanical alloying significantly influence the phase reactions occurring between the three elements (Ti, Mg, and Si) as compared with the as-blended powder. Mixing, fracturing and welding of the powder particles during MA lead to intimate mixing of the elements on an atomic level and extension of the solubility limit of magnesium and silicon in the titanium hydride. Almost all the magnesium and silicon are dissolved in the titanium hydride matrix during mechanical alloying and this supersaturated solid solution is stable on heating to 350°C. An increase in solubility of magnesium in titanium due to mechanical alloying was observed earlier [14,15], with a maximum solubility of 1.9 wt% achieved. Therefore, use of titanium hydride instead of titanium in the present work allowed us to increase the solubility of magnesium considerably. This can be due to at least two reasons. Firstly, the face-centertetragonal (fct) titanium hydride lattice is more open than the hexagonal-close-packed (hcp) titanium lattice, as the atom packing efficiencies are 0.64 and 0.75, respectively [16]. Secondly, the crystal size of mechanically milled titanium hydride is generally much smaller and the strain content is higher than that of mechanically milled titanium after the same milling time [11]. Shorter circuit diffusion paths, which enhance diffusion, are present in the milled titanium hydride powder compared to the milled titanium powder, thus providing better mixing of elements on the atomic level.

The endothermic peaks near 350 and 590°C evidently result from overlapping of a wide endothermic peak (within the temperature range 300–600°C), which is due to titanium hydride decomposition, with a wide exothermic peak (within the temperature range 350-590°C). This exothermic peak, with an onset at 360°C and maximum at 430°C, results from several phase reactions: decomposition of the supersaturated solid solution of magnesium and silicon in titanium hydride, reaction of the silicon with magnesium (in a lower temperature range) leading to formation of the magnesium silicide (Mg₂Si) and reaction of the silicon with titanium (at higher temperatures) leading to formation of the titanium silicide (Ti₅Si₃). The temperatures of the phase formations are much lower than in the as-mixed powders, which may be due to kinetic factors such as a decrease in the activation energy barriers in the mechanically alloyed powder. After heating to 600°C, the supersaturated solution in the titanium hydride decomposes almost completely producing titanium, magnesium and titanium silicides, and magnesium precipitates. The wide XRD peaks from magnesium observed after annealing at 600°C (see Fig. 4e) indicate a very fine precipitation size. Since some silicon reacts with titanium in the mechanically alloyed powders in this temperature range, some magnesium is left unreacted, and a Mg-Mg₂Si eutectic is produced, with a melting temperature of 638°C (see Fig. 5). Melting of the eutectic results in reaction of liquid silicon with titanium, resulting in an increase in the volume fraction of the Ti₅Si₃ phase. This reaction appears to be responsible for the exothermic peak near 640°C observed in the DTA curve from the MA powders (see Fig. 3). In accordance with the phase diagram in Fig. 5, removing silicon from the melt should also accelerate the decomposition of the magnesium silicide. No XRD peaks from Mg₂Si and Mg are detected in the system at a temperature of 660°C and above, although the intensity of the Ti₅Si₃ peaks continuously increases and peaks from magnesium oxide appear within the temperature range 660 to 900°C, suggesting that a liquid phase containing Mg and Si is still present in the system in this temperature range. The results indicate that, in contrast to the situation with as-blended powder, the magnesium silicide formed in the MA powder is stable only at temperatures below 630°C. A wide exothermic peak above 900°C may correspond to the reaction of fine titanium powder with contaminant nitrogen present in the argon used in the DTA. Some contamination during MA may also be present [18]. The final composition of the powder after heating to 1150°C is Ti₅Si₃, TiN_{0.3} and MgO. The absence of XRD peaks from the titanium nitride in the

as-blended powder can be explained by the much larger size of the powder particles and, therefore, lower surface area. In fact, the initial particle size of the titanium hydride was ~250 μ m, while after mechanical alloying the particle size was less than 5 μ m, indicating that the surface area of the particles increased at least 1.4×10³ times.

5. Conclusions

DTA and XRD analyses of phase reactions and phases occurring during heating to 1150° C in both as-blended and mechanically alloyed powders (80 wt% TiH₂+12 wt% Mg+8 wt% Si) were conducted. The following conclusions can be made.

- 1. Heat treatment of the as-blended powder leads to formation of four phases: Mg₂Si, Ti₅Si₃, MgO and Ti. Formation of Ti is due to decomposition of the titanium hydride and hydrogen degassing and is accompanied by an endothermic peak on the DTA curve with an onset at 563°C and minimum at 638°C. The magnesium silicide is formed by an exothermic reaction of magnesium and silicon with an onset at 483°C and a peak at 510°C. This phase is stable during subsequent heating up to 950°C, where it starts to decompose into a liquid solution of magnesium in silicon. The liquid silicon reacts exothermically with titanium and the liquid magnesium oxidizes, resulting in formation of, respectively, Ti₅Si₃ and MgO. There were only three stable phases in the system after heating to 1150°C: Ti₅Si₃, MgO and Ti. No reactions occurred during subsequent cooling and a second heating.
- Mechanical alloying of the blended powders leads to formation of a supersaturated solid solution of magnesium and silicon in the titanium hydride matrix which is stable on heating to 350°C.
- 3. Heat treatment of the mechanically alloyed powder leads to formation of six phases: Ti, Mg, Mg₂Si, Ti₅Si₃, MgO and TiN_{0.3}. Decomposition of the titanium hydride occurs in the temperature range 350 to 590°C, i.e. at lower temperatures than in the case of the as-blended powder. This decomposition produces titanium, magnesium silicide, titanium silicide and precipitation of magnesium from the supersaturated solid solution. The magnesium silicide is stable only at temperatures below 640°C. Above this temperature it decomposes followed by reaction of the silicon with titanium and oxidation of magnesium. The rest of the titanium reacts with contaminant nitrogen present in the argon used in the DTA. The final composition of the mechanically alloyed powder after heating to 1100°C is Ti₅Si₃, MgO, and TiN_{0.3}
- Ti₅Si₃, MgO and Ti are thermodynamically stable phases in the Ti-Mg-Si system within the temperature

range 20 to 1100°C. Magnesium silicide is a stable phase in this system only at temperatures below 640°C.

Acknowledgements

This work was partially supported by the US Army Research Office (Dr. W.M. Mullins), contract No. DAAG55-98-1-0008, and the National Science Foundation (Dr. B.A. MacDonald), grant No. DMR-9901642.

References

- C.M. Ward-Close, F.H. (Sam) Froes, S.S. Cho, Synthesis and processing of light weight metallic materials — an overview, in: C.M. Ward-Close, F.H. (Sam) Froes, S.S. Cho, D.L. Chellman (Eds.), Synthesis/Processing of Light Weight Metallic Materials, Vol. II, TMS, Warrendale, PA, 1997, pp. 1–15.
- [2] J.C. Ekvall, J.E. Rhodes, G.G. Wald (Eds.), Design of Fatigue and Fracture Resistant Structures, ASTM Special Publication 761, ASTM, Philadelphia, 1982, pp. 328–336.
- [3] J.L. Murray, Si-Ti (silicon-titanium), in: Binary Alloy Phase Diagrams, ASM, Metals Park, OH, 1987, pp. 3367–3371.
- [4] S. Suryanarayana, D. Eliezer, F.H. Froes, Synthesis, properties and applications of titanium aluminides, J. Mater. Sci. 27 (1992) 5113– 5140.
- [5] P.W. Powell, G.H. Reynolds, Gamma titanium aluminide composite development activities, in: F.H. (Sam) Froes (Ed.), P/M in Aerospace, Defense and Demanding Applications — 1993, MPIF, Princeton, NJ, 1993, pp. 291–297.
- [6] O.N. Senkov, F.H. (Sam) Froes, E.G. Baburaj, Development of nanocrystalline titanium aluminade–titanium silicide particulate composite, Scripta Mater. 37 (1996) 575–579.
- [7] A.M. James, M.P. Lord, Macmillan's Chemical and Physical Data, Macmillan, London, UK, 1992.
- [8] C.M. Ward-Close, P.G. Partridge, P. Holdway, A.W. Bowen, An X-ray diffraction study of vapour quenched titanium magnesium alloys, in: F.H. (Sam) Froes, I.L. Caplan (Eds.), Titanium'92: Science and Technology, TMS, Warrendale, PA, 1993, pp. 659–666.
- [9] C.M. Ward-Close, P.G. Partridge, C.J. Gilmore, Precipitation in titanium–magnesium and titanium–calcium alloys, in: F.H. (Sam) Froes, I.L. Caplan (Eds.), Titanium'92: Science and Technology, TMS, Warrendale, PA, 1993, pp. 651–658.
- [10] C.M. Ward-Close, P.G. Partridge, The production of titanium magnesium alloys by vapour quenching, Mater. Lett. 11 (1991) 295–300.
- [11] E. Zhou, Development of low density Ti-Mg alloys, MS Thesis, University of Idaho, Moscow, ID, USA, 1994.
- [12] N. Srisukhumbowornchai, Microstructural control in Ti–Al alloys, MS Thesis, University of Idaho, Moscow, ID, USA, 1997.
- [13] A.D. McQuillan, An experimental and thermodynamic investigation of the hydrogen-titanium system, Proc. R. Soc. London A 204 (1951) 309–323.
- [14] E. Zhou, C. Suryanaryana, F.H. (Sam) Froes, Mechanical alloying of titanium-magnesium powders, in: P.A. Blenkinsop, W.J. Evans, H.M. Flower (Eds.), Titanium'95: Science and Technology, Institute of Materials, London, 1996, pp. 2657–2664.
- [15] E. Zhou, C. Suryanaryana, F.H. (Sam) Froes, Effect of pre-milling elemental powders on solid solubility extension of magnesium in titanium by mechanical alloying, Mater. Lett. 23 (1995) 27–31.
- [16] A. San-Martin, F.D. Manchester, The hydrogen-titanium system, in: J.L. Murray (Ed.), Phase Diagrams of Binary Titanium Alloys, ASM International, Materials Park, OH, 1987, pp. 123–125.

- [17] A.A. Nayeb-Hashemi, J.B. Clark, Mg–Si (magnesium–silicon), in: Binary Alloy Phase Diagrams, ASM International, Materials Park, OH, 1987, pp. 2547–2549.
- [18] P.S. Goodwin, D.K. Mukhopadhyay, C. Suryanarayana, F.H. Froes,

C.M. Ward-Close, Control of interstitial contamination during mechanical alloying of titanium based materials, in: P.A. Blenkinshop, W.J. Evans, H.M. Flower (Eds.), Titanum'95: Science and Technology, Institute of Materials, London, 1996, pp. 2626–2633.