

# EFFECT OF Cu ON THE SINTERING ABILITY OF A SURFACE MODIFIED $\text{Ti}_5\text{Si}_3$ -BASED ALLOY SYNTHESIZED BY MECHANICAL ALLOYING

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**Abstract.** A  $(\text{Ti,Mg})_5\text{Si}_3$  alloy was synthesized by mechanical alloying from  $\text{TiH}_{1.924}$ , Mg and Si powders. After milling, the surface of a portion of the powder was chemically modified by the deposition of a Cu thin layer by d.c. magnetron sputtering. Coated and uncoated samples were consolidated by cold isostatic pressing and sintered at different temperatures. The  $(\text{Ti,Mg})_5\text{Si}_3$  phase formed through milling decomposed into  $\text{Ti}_5\text{Si}_3 + \text{Mg}_2\text{Si}$  during sintering at 900 °C. After 1300 °C sintering, the coated and uncoated samples were formed mainly by a  $\text{Ti}_5\text{Si}_3$  intermetallic phase. MgO fine precipitates were also detected in the microstructure of the samples sintered at 1300 °C. Cu acted as an activating sintering element for reaching densification.

## 1. INTRODUCTION

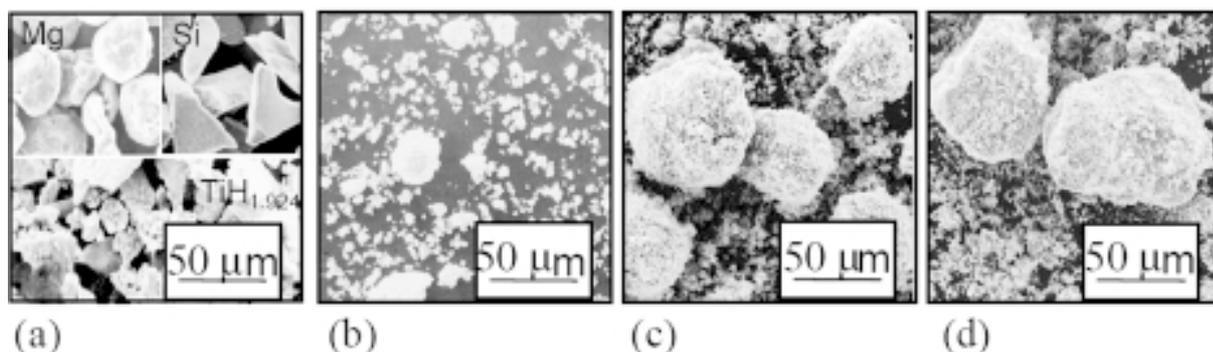
In the aerospace industry, the choice of materials allowing a weight reduction of the components is extremely important. Titanium-based alloys are suitable materials for this kind of applications, since they have low density, good corrosion resistance and high strength to weight ratio [1]. In order to obtain even lower densities, one of the possibilities is to add to titanium some lighter materials as magnesium, silicon or aluminum [2]. In a previous work, mechanical alloying (MA) was used as synthesis technique to produce a  $\text{Ti}_{60}\text{Mg}_{10}\text{Si}_{30}$  sample by two routes from: (i) elemental Ti, Mg and Si and (ii)  $\text{TiH}_{1.924}$ , Mg and Si powders [3]. However, the compaction of intermetallic powders is a hard task since they present low ductility and fracture-toughness. Moreover, the melting points of these materials are generally high which turns the process even more difficult to perform. In order to overcome this problem, a new method for powders surface

modification has been proposed [4] in which sputtering is used to deposit metallic thin layers (few micrometers thickness) on the surface of the powders with the aim of facilitating their compaction and sinterability, as well as final mechanical properties, eg. fracture-toughness. In the present work, a  $(\text{TiH}_{1.924})_{55}\text{Mg}_{10}\text{Si}_{35}$  mixture was mechanically alloyed in a planetary ball mill from  $\text{TiH}_{1.924}$ , Mg and Si powders. Surface of a part of the milling product was subsequently modified by a sputtered deposited Cu thin layer. Coated and uncoated mixtures were finally compacted at room temperature by Cold Isostatic Pressure (CIP) and sintered at different temperatures. The results will be compared and discussed in terms of final structure and porosity.

## 2. EXPERIMENTAL

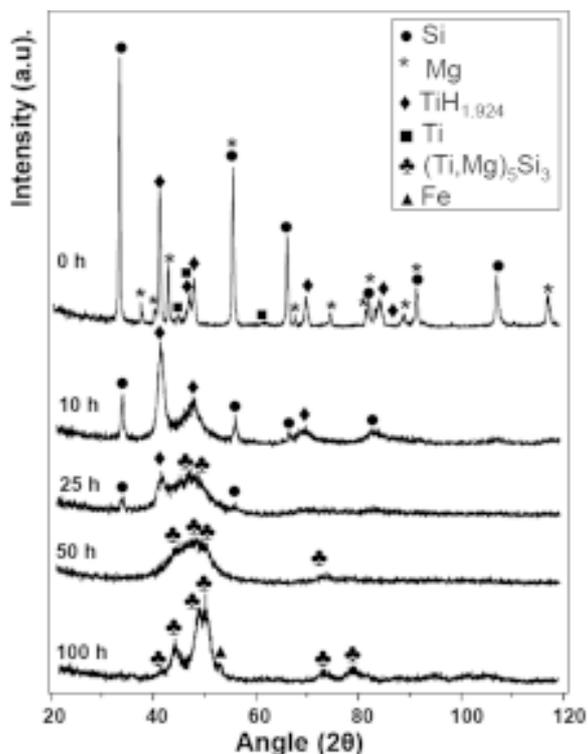
A  $(\text{TiH}_{1.924})_{55}\text{Mg}_{10}\text{Si}_{35}$  mixture was mechanically alloyed in a planetary ball mill (Fritsch Pulverisette

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**Fig. 1.** Scanning electron micrographs of: (a) as-blended powder mixture, (b) 10 h MA, (c) 50 h MA, and (d) 100 h MA.

6) from  $\text{TiH}_{1.924}$ , Si, and Mg powders. Hardened steel vial (250 ml) and balls (20 mm diameter) were used in the process. MA was performed in a hydrogenated argon atmosphere in order to prevent contamination. A ball to powder weight ratio of 20:1 and a rotation speed of 300 rpm were selected. After 15 min of milling, the process was interrupted for 5 min to cool the vial and to reverse the rotation movement. Small quantities of powder were withdrawn from the vial after 10, 25, 50, and 100 h (maximum milling time) for analysis. A portion of the mixture milled for 100 h was subsequently coated with Cu by d.c. magnetron sputtering, with a specific discharge power of  $1.2 \cdot 10^{-2} \text{ W/mm}^2$  for 3 h. The depositions were performed in a pure argon atmosphere ( $5 \cdot 10^{-3} \text{ Pa}$ ) after the chamber evacuation down to an ultimate pressure of  $10^{-6} \text{ Pa}$ . During the deposition, the powders were continually shaken by vibration and translation movements in order to obtain coatings as homogeneous as possible. The powders obtained by MA, with and without Cu-coating, were cold isostatic pressed at 330 MPa during 15 min. The green compacts were subsequently sintered in vacuum during 12 h at different temperatures (900, 1100, and 1300°C). X-ray diffraction (XRD) with  $\text{Co-K}_\alpha$  radiation, electron probe microanalysis (EPMA) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) analysis were used for structural, morphological and chemical composition characterization. The open porosity was determined by mercury porosimetry using a Micromeritics 9320 equipment. Particle size distributions were determined by laser scattering (Coulter LS 130 equipment).



**Fig. 2.** XRD patterns of the powders mixture as a function of milling time.

### 3. RESULTS AND DISCUSSION

Fig. 1 shows scanning electron micrographs of the as-blended and mechanically alloyed mixtures. As can be seen, after 10 h of milling there was already a significant decrease of the particles size, characteristic for fracture process. For longer periods of milling time (50 and 100 h) some big particles were detected. However, the fraction of these particles was relatively small as confirmed by the particle size distributions obtained from the as-

**Table 1.** Chemical composition of the sintered samples obtained by EPMA.

		Ti (at.%)	Mg (at.%)	Si (at.%)	Cu (at.%)
$(TiH_{1.924})_{55}Mg_{10}Si_{35}$	900 °C	55.2	8.4	36.4	-
	1100 °C	56.3	7.5	36.2	-
	1300 °C	57.5	6.4	36.1	-
$(TiH_{1.924})_{55}Mg_{10}Si_{35}$ + Cu	1100 °C	51.5	3.7	37.2	7.6
	1300 °C	59.5	0.2	39.7	0.6

**Table 2.** Porosity measurements results for sintered samples at 1100 and 1300°C.

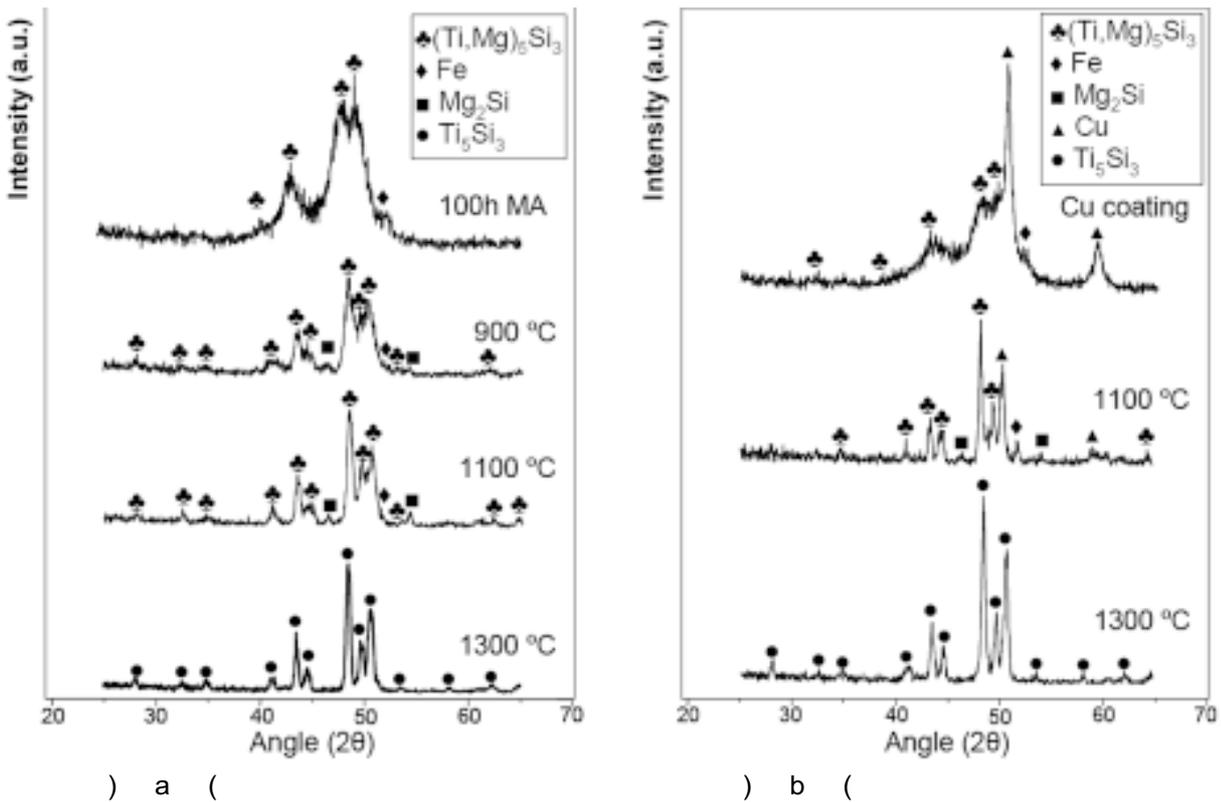
	Sintering Temperature (°C)	Porosity (%)
$(TiH_{1.924})_{55}Mg_{10}Si_{35}$	1100	30.8
	1300	30.7
$(TiH_{1.924})_{55}Mg_{10}Si_{35}$ + Cu	1100	28.6
	1300	4.2

blended and 100 h MA'ed mixtures ( $dp_{50}$  values of 152, and 5  $\mu$ m, respectively).

Fig. 2 shows the structural evolution of the powders as a function of milling time. The as-blended mixture is formed by the tetragonal  $TiH_{1.924}$ , hcp-Mg, and fcc-Si phases. Weak diffraction lines were also detected at  $2\theta = 45, 47,$  and  $62.4^\circ$ , ascribed to the  $\alpha$ -Ti phase. This indicates the presence of some elemental Ti in the  $TiH_{1.924}$  powder. After 10 h of milling, the XRD peaks of the hcp-Mg phase, and some of the fcc-Si phase, are no longer visible, meaning that these elements substitute Ti in the tetragonal  $TiH_{1.924}$  lattice leading to the formation of a  $TiH_{1.924}(Mg,Si)$  solid solution. The XRD pattern of the 25 h milled sample shows the formation of the  $(Ti,Mg)_5Si_3$  intermetallic, coexisting with  $TiH_{1.924}(Mg,Si)$  solid solution. For  $t=50$  h, the milled powders are formed only by the  $(Ti,Mg)_5Si_3$  phase. For longer milling times (up to 100 h) an increase of the grain size of the  $(Ti,Mg)_5Si_3$  intermetallic phase occurred. This means that the titanium hydride solid solution decomposed during milling (hydrogen degassing) and later reacted with silicon to form the intermetallic  $(Ti,Mg)_5Si_3$ . This result is in accordance with the previous study on this system [3]. After 100 h milling, vestiges of  $\alpha$ -Fe phase were detected in the XRD pattern, meaning that a contamination from the vial and balls occurred during the synthesis process [5].

Fig. 3 shows the XRD patterns of the uncoated and coated samples in the as-milled condition and after sintering at different temperatures. As ex-

pected, when compared with the uncoated powder, the XRD pattern of the coated powder has additional diffraction peaks ascribed to the fcc-Cu phase. During sintering at low temperature, the  $(Ti,Mg)_5Si_3$  intermetallic phase formed through milling, decomposed into  $Ti_5Si_3 + Mg_2Si$ . These structures co-exist even after sintering at 1100 °C, although in this case the peaks are better defined as the result of a grain size increase. Furthermore, XRD peaks of the fcc-Cu phase are still present in the XRD pattern of the 1100 °C sintered coated sample. After sintering at 1300 °C (maximal sintering temperature used) all the XRD peaks of both samples (with and without Cu coating) belong to the  $Ti_5Si_3$  phase. In fact the chemical composition results (Table 1) showed a significant decrease of Mg and Cu contents in the coated samples sintered at 1300 °C. It should be noted that this temperature is much higher than the melting points of the fcc-Cu and  $Mg_2Si$  phases (1080 and 1085 °C, respectively). The reason why the Mg content decreased during sintering much more in the coated sample than in the uncoated sample requires further investigation. Therefore, one may say that similar structures were obtained for both samples (coated and uncoated) after 1300 °C sintering. However, taking into account the results of open porosity (Table 2) one might say that Cu played an important role on the sintering behavior of the milled  $(TiH_{1.924})_{55}Mg_{10}Si_{35}$  mixture. In fact, a strong decrease of the porosity occurred in the Cu coated sample sintered at 1300 °C. This element acted



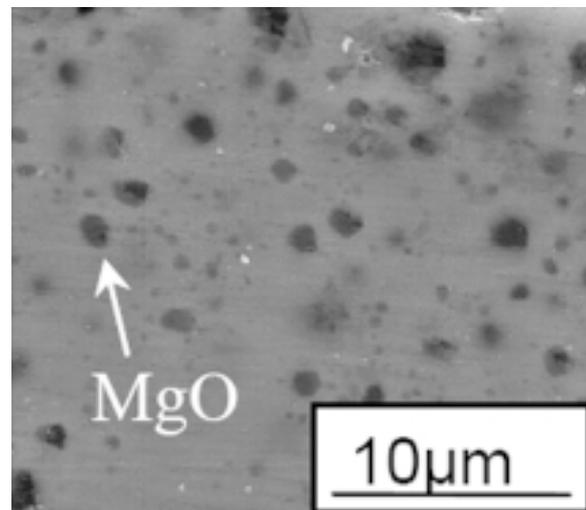
**Fig. 3.** XRD patterns of the (a) uncoated and (b) coated samples in the as-milled condition and after sintering at different temperatures.

as a temporary sintering adding element at temperatures between 1100 and 1300 °C.

Fig. 4 shows SEM micrographs of uncoated and coated samples sintered at 1300 °C. The lower magnification images confirm that the lower open porosity results from the positive role of Cu in the sintering behavior of the mechanically alloyed powders. In both samples, some precipitates were detected in the sintered zones (Fig. 4) which, by EDS analysis, were identified as MgO. This phase could not be detected by X-ray analysis since its two stronger diffraction peaks are positioned at  $2\theta = 50.42^\circ$  and  $74.08^\circ$ , superimposed with the diffraction peaks of the  $Ti_5Si_3$  phase.

#### 4. CONCLUSIONS

Magnetron sputtering was used to deposit a Cu thin layer on the surface of  $Ti_5Si_3$  intermetallic powders synthesized by mechanical alloying from  $TiH_{1.924}$ , Mg and Si powders. The results showed that the  $(Ti,Mg)_5Si_3$  intermetallic phase



**Fig. 4.** SEM micrograph of sample sintered at 1300 °C.

formed during milling decomposed into  $Ti_5Si_3 + Mg_2Si$  during sintering at 900 °C. For 1300 °C sintering, both samples (coated and uncoated) consisted mainly of the phase  $Ti_5Si_3$ . In the better consolidated areas of the compacts sintered at 1300

°C, some MgO fine precipitates were also detected. Cu acted as an activating sintering element for reaching densification.

### ACKNOWLEDGEMENTS

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### REFERENCES

[1] *Titanium and Titanium Alloys*, ed. by

C. Leyens and M. Peters (Wiley-VCH, 2003).

[2] C. Suryanarayana // *Prog. Mater. Sci.* **46** (2001) 1.

[3] L. Dias, B. Trindade, C. Coelho, S. Patankar, C. Draney and F.H. Sam Froes // *Mater. Sci. Eng. A* **364** (2004) 273.

[4] F. Simões and B. Trindade // *Mater. Sci. Eng. A* **397** (2005) 257.

[5] M. Oehring, Z. H. Yan, T. Klassen and R. Bormann // *Phys. Status Solidi A* **131** (1992) 671.