Rev.Adv.Mater.Sci. 21(2009) 173-182

EFFECT OF Ni AND Cu INTERMEDIATE LAYERS ON THE SINTERABILITY OF A Ti-35SI-10MG (% AT.) MIXTURE SYNTHESIZED BY MECHANICAL ALLOYING

M. Caetano[1], F.J. Oliveira[2], R.F. Silva[2], F. Simões[1] and B. Trindade[1]

[1]CEMUC, Mechanical Engineering Department, University of Coimbra, Polo II, 3030-788 Coimbra, Portugal
[2]CICECO, Ceramics and Glass Engineering Department, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Received: January 15, 2009

Abstract. A Ti-35Si-10Mg (at.%) mixture was synthesized by mechanical alloying from Ti, Mg, and Si elemental powders. After milling the surface of the particles was chemically modified by the deposition of Ni and Cu thin layers by d.c. magnetron sputtering. Coated and uncoated particles were subsequently consolidated by two different routes: (i) cold isostatic pressing followed by pressureless sintering at T = 1300 °C in vacuum and (ii) cold isostatic pressing followed by hot isostatic pressing at T = 900 °C with an applied pressure of 1500 MPa. The results showed that all samples were formed by a final Ti_3Si_5 + Mg_2Si microstructure. Cu and Ni existed as single phases after hot isostatic pressing. Ni and Cu coatings acted as auxiliary sintering elements during compaction of the mechanically alloyed Ti-35Si-10Mg powders, giving rise to better final compacts. The higher values of hardness and Young's modulus were obtained for the HIP'ed coated samples, as result of their better densification.

1. INTRODUCTION

Synthesis of intermetallic compounds with high melting points has been investigated in many studies. Among the intermetallics considered for high temperature applications, Ti_5Si_3 is one of the most adequate compounds because of its high melting point (2130 °C), room temperature toughness, high temperature strength and creep resistance, oxidation resistance, and relatively low density (4.32 $g \cdot cm^{-3}$). Different techniques have been used for the synthesis of Ti_5Si_3 bulk materials such as arc melting [1], hot isostatic pressing [2-7], modified hot pressing [8], explosion [9] and, more recently, electro-discharge-sintering [10]. These techniques have been applied to elemental or prealloyed particles. Mechanical alloying has been used in numerous studies to synthesize Ti_5Si_3 powder, see for instance [3,4,11]. This technique provokes the initiation of highly exothermic reactions, which is the case of the Ti_5Si_3 formation from Ti and Si elemental particles. The formation of this intermetallic is associated to a high heat of reaction of -577.4 kJ mol^{-1}.

Full dense consolidation of particles with intermetallic structures such as Ti_5Si_3 is a hard task as these materials present low deformation ability and high melting points, requiring elevated temperatures of sintering and high applied pressures. This normally leads to the appearance of cracks with consequent implication in the properties of the final product. One possible way to overcome this problem is the chemical modification of the surface of the intermetallic particles before the consolidation process. In previous work [3] the authors proposed the use of a PVD process (magnetron sputtering) for the deposition of thin layers (some

Corresponding author: B. Trindade, e-mail: bruno.trindade@dem.uc.pt

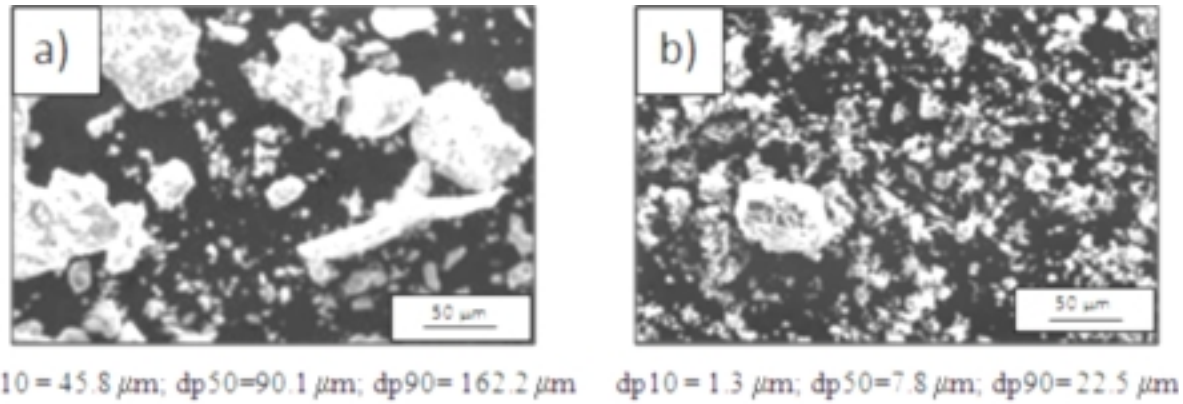

Fig. 1. Morphology of the particles before (a) and after (b) 100 h of mechanical alloying and corresponding characteristic d*p* values (dp_{10}, dp_{50}, and dp_{90}) obtained from the particles size distribution curves.

micrometers thick) of ductile metallic elements, with substantially lower melting points compared to the ones of the intermetallic compounds. The results obtained so far clearly showed that the deposition of a transition metal, in particular aluminium, on the surface of TiAl- and Ti_5Si_3-based intermetallic powders leads to an improvement of the mechanical properties of the final compacts by decreasing the final porosity and by improving the deformation ability of the surface of the particles. Moreover, lower sintering temperature and working pressures are required, decreasing the risk of cracking.

In this work, we studied the influence of the deposition of Ni and Cu thin layers on the surface of Ti-35Si-10Mg (at.%) intermetallic particles synthesized by mechanical alloying from elemental Ti, Mg, and Si powders. Mg was introduced to decrease the final density of the compact.

2. EXPERIMENTAL DETAILS

A Ti-35Si-10Mg (at.%) alloy was synthesized by mechanical alloying from Ti, Mg, and Si particles. Milling was performed in a planetary ball mill for a maximum time of 100h using hardened steel vial and 15 balls of 20 mm diameter. The milling procedure was interrupted each 15 min, for 10 min, to cool down the system. A ball-to-powder weight ratio of 20:1 was chosen and the milling intensity was adjusted to 200 rpm. In order to avoid contamination, milling was performed in a hydrogenated argon atmosphere (5% H_2) and was interrupted after selected times to take out small amounts of powder for analysis.

After milling, the surface of the powders was chemically modified by the deposition of Ni and Cu thin layers by d.c. magnetron sputtering with a specific discharge power of $2.2 \cdot 10^{-2}$ W/mm^2 for 60 min. The depositions were performed in a pure argon atmosphere (0.5 Pa) after the chamber had been evacuated down to a base pressure of 10^{-4} Pa. During the depositions the particles were continually shaken by vibration and translation movements in order to obtain homogeneous coatings.

Coated and uncoated samples were therefore consolidated by two different routes: (i) cold isostatic pressing (CIP) at 320 MPa followed by pressureless sintering at *T* = 1300 °C in vacuum and (ii) CIP followed by hot isostatic pressing (HIP) at *T* = 900 °C with an applied pressure of 150 MPa.

Particle size distributions were determined by laser scattering from a powder suspension in water, under mechanical agitation after a 60-second sonication. The milled particles and the final compacts were analyzed using by the following techniques: X-ray diffraction (XRD) with Co *K*a radiation for structural analysis, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) and electron probe microanalysis (EPMA) for morphological and chemical composition analysis, He picnometry for samples density determination and mercury porosimetry for evaluation of porosity. The hardness and Young´s modulus were calculated by micro and ultramicrohardness with 4.9 N and 0.245 N loads,

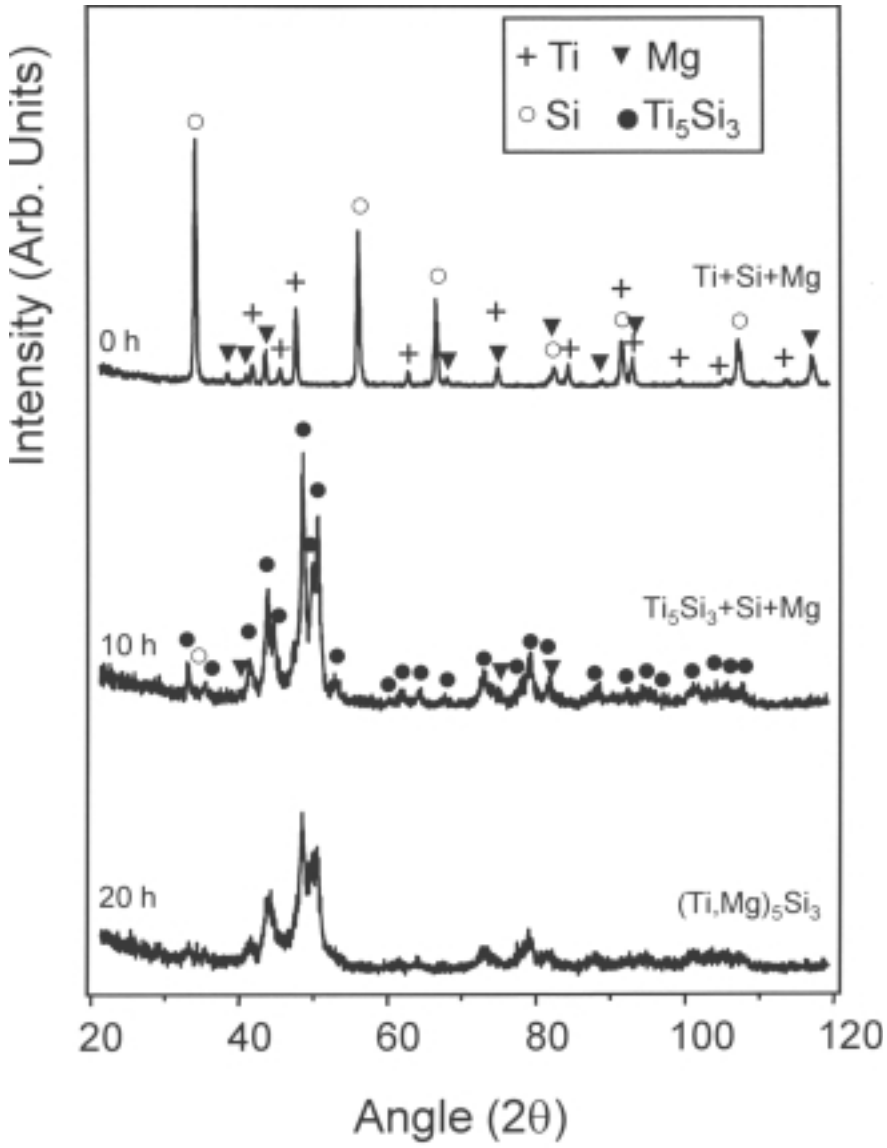

Fig. 2. XRD patterns of the Ti-35Si-10Mg mixture as a function of milling time.

respectively, according to the method described in [12].

3. EXPERIMENTAL RESULTS

3.1. Mechanical alloying

Fig. 1 shows the morphology of the particles before and after mechanical alloying as well as the corresponding characteristic d*p* values (dp_{10}, dp_{50} and dp_{90}) obtained from the particles size distribution curves. As can be seen, the starting mixture is characterized by a relatively large distribution with a median particle size (dp_{50}) of 90.1 mm. In the first hours of synthesis there is a tendency for the formation of particles with quite different sizes. With the increase of time this tendency is more notorious. After 100 h of milling, the distribution is very broad with characteristic d*p* values lower than the ones of the initial distribution (dp_{50} of 7.8 μm). This behavior is typical of brittle systems and can be explained by the formation of intermetallic phases during milling. In fact, X-ray diffraction analysis performed on the milled particles (Fig. 2) shows that after 20 h of synthesis the intermetallic hcp Ti_5Si_3 was already formed. No diffraction peaks of the α-Mg phase could be detected meaning that

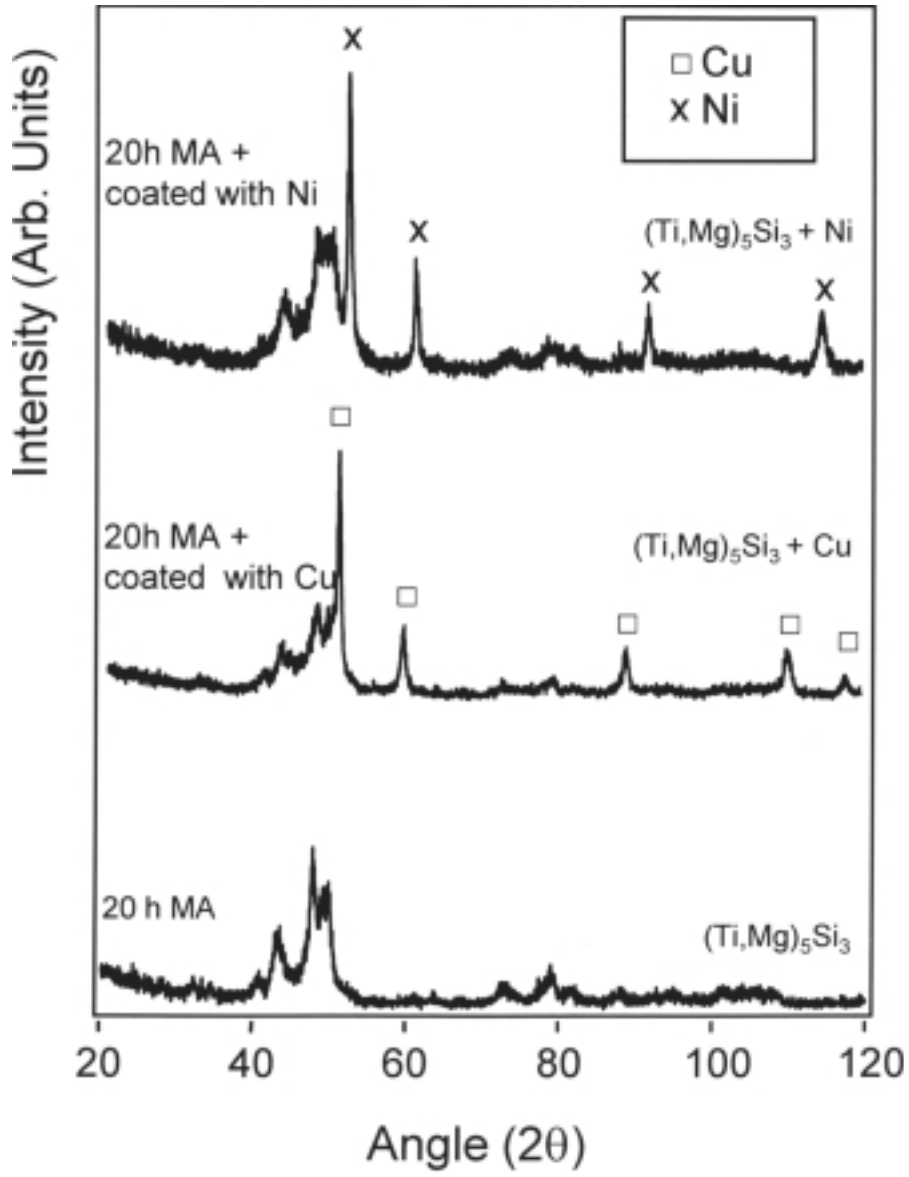

Fig. 3. XRD patterns of the coated and uncoated Ti-35Si-10Mg mixture milled for 20h.

this element was incorporated in the intermetallic phase, probably in substitutional positions, giving rise to a mixed $(Ti,Mg)_5Si_3$ intermetallic phase. The lattice parameters *a* and *c* of this phase measured after 20h of milling are of 7.49 and 5.23 Å, respectively, which corroborate the hypothesis of a mixed intermetallic compound formation. In fact, these values are slightly higher than the ones of the standard hexagonal Ti_5Si_3 compound, i.e. *a* = 7.46 Å and *c* = 5.15 Å [13]. Expansion of the lattice is in accordance with the substitution of Ti (at. radius = 1.47 Å) by Mg (at. radius = 1.60 Å). The grain size of the $(Ti,Mg)_5Si_3$ phase after 20 h of milling was of about 18 nm. This value was obtained from the FWHM of the XRD diffraction peaks of this phase. No structural changes were observed for further milling time up to 100 h. However, an increase of the grain size of the $(Ti,Mg)_5Si_3$ phase occurred (90 nm after 100 h milling, against 18 nm after 20h milling).

3.2. Sputtering coatings

After mechanical alloying, the powders were coated by Cu and Ni. The X-ray diffraction patterns of the uncoated and coated particles are presented in

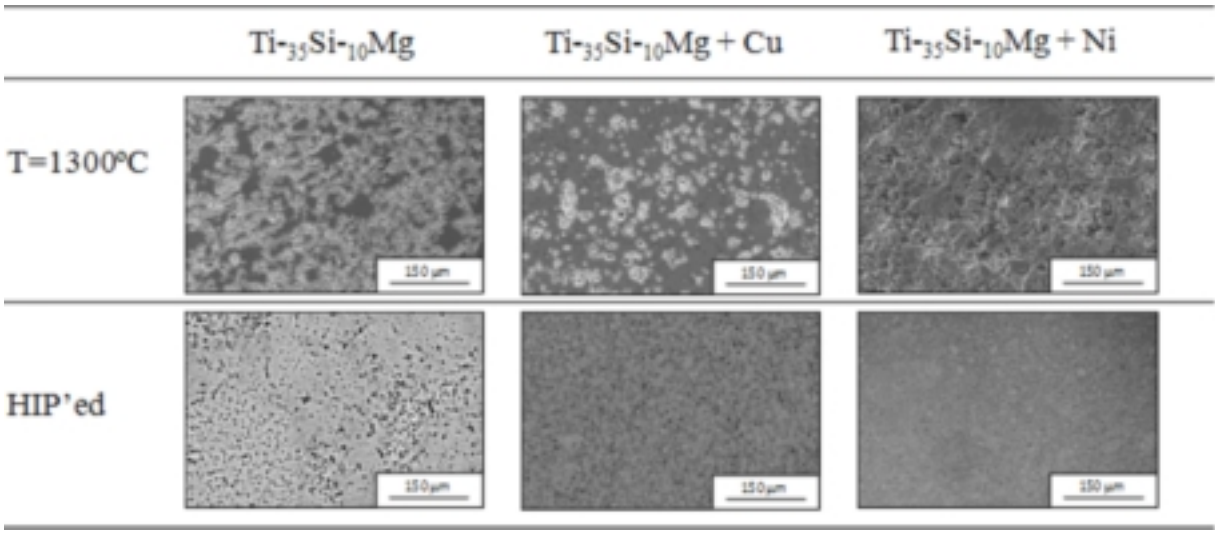

Fig. 4. Morphology of the coated and uncoated Ti-35Si-10Mg samples sintered at 1300 °C and HIP'ed.

Table 1. Density and porosity of the coated and uncoated Ti-35Si-10Mg samples sintered at two different temperatures and HIP'ed.

		Density, g cm^3	Porosity, %
Ti-35Si-10Mg	1100 °C	4.31	17
	1300 °C	4.34	15
	HIP	4.4	10
Ti-35Si-10Mg+Cu	1100 °C	4.35	14
	1300 °C	4.31	10
	HIP	4.37	1
Ti-35Si-10Mg+Ni	1100 °C	4.36	15
	1300 °C	4.33	12
	HIP	4.41	3

Fig. 3. Quite narrow peaks of the Cu and Ni fcc phases are clearly visible in the XRD patterns of the coated samples, (ICDD cards nº 85-1326 [14] and 04-0850 [15], respectively), meaning that sputtering gave rise to crystalline equilibrium structures.

3.3. Particles consolidation

The coated and uncoated particles were consolidated by two different routes: (i) CIP followed by pressureless vacuum sintering at 1100 °C and 1300 °C and (ii) CIP followed by HIP at 900 °C with an applied pressure of 150 MPa. The values of density and porosity of the final compacts are presented in Table 1. Fig. 4 shows the micrographs of the samples sintered at 1300 °C and HIP'ed. As can be seen, CIP followed by pressureless sintering gave rise to compacts with a high number of pores, i.e. with a low density, in particular for the uncoated sample sintered at the lowest temperature (1100ºC). Cu and Ni coatings slightly improved the sinterability of the samples. Concerning the HIP'ed samples the situation is quite different. Whilst the uncoated sample shows a significant high number of pores (10% of porosity) the samples coated with Cu and Ni are quite dense with porosities of 1 and 3%, respectively. These results clearly show that these two elements play an important role on the sinterability of the mechanically alloyed Ti-35Si-10Mg (% at.) particles, acting as sintering aids and therefore improving densification of the compacts.

The micrographs of the HIP'ed coated samples show zones with different shades. EDS analysis revealed that, in both cases, the brighter particles correspond to phases rich in Cu and Ni, meaning that these elements segregated during sintering (Fig. 5). These particles are of higher dimension in the case of the Cu-coated HIP'ed sample (few tens of micrometers). Similarly to the observations of Park et al. [16] from a reactive-sintered Ti_5Si_3 sample, Kang *et al.* [9] also refer segregation of Cu in a Ti_5Si_3-Cu sample obtained by explosion synthesis.

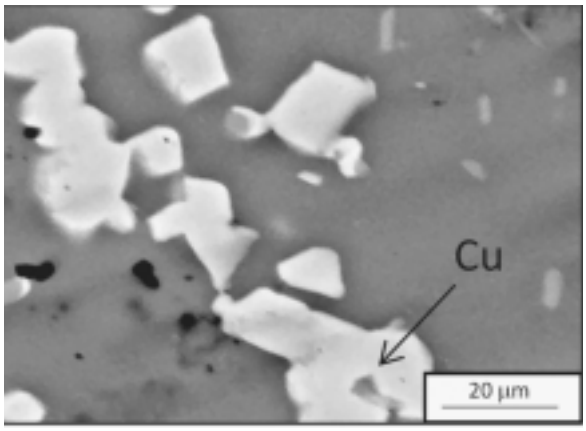

Fig. 5. Morphology (BSE-SEM image) of the Ti-35Si-10Mg-Cu HIP'ed sample showing segregation of Cu.

Table 2. Chemical composition of the coated and uncoated Ti-35Si-10Mg samples sintered at two different temperatures and HIP'ed.

		Ti (at.%)	Mg (at.%)	Si (at.%)	Cu or Ni (at.%)	(Fe+C+O) (at.%)
Ti-35Si-10Mg	1100 °C	52.2	6.9	33.6	-	7.3
	1300 °C	53.9	6.0	33.9	-	6.2
	HIP	53.0	6.2	33.3	-	7.5
Ti-35Si-10Mg+Cu	1100 °C	47.5	3.4	34.3	7.0	7.8
	1300 °C	54.6	0.2	36.4	0.5	8.3
	HIP	50.5	3.0	34.1	6.4	6.0
Ti-35Si-10Mg+Ni	1100 °C	51.5	5.8	31.2	8.2	3.3
	1300 °C	53.9	1.8	33.1	6.0	5.2
	HIP	51.1	6.0	31.5	7.5	3.9

In order to understand the structural role of Cu and Ni on the sinterability of the studied samples, XRD analysis was performed on the final compacts. The results are shown in Fig. 6. No important structural changes occurred during consolidation of the samples. Peaks of the Cu and Ni fcc phases still exist in the 1100 °C sintered and HIP'ed samples, suggesting a low solubility of these elements in the Ti_5Si_3 intermetallic compound.

The only phase formed during heating was the Mg_2Si intermetallic, which is present in all samples sintered at 1100 °C and HIP'ed. In fact, as observed in previous work [17], the increase of temperature provokes the exit of magnesium from the $(Ti,Mg)_5Si_3$ phase formed during mechanical alloying, this element reacting with Si to form the Mg_2Si phase. This phase was not longer detected after sintering at 1300 °C. The chemical composition of the final compacts (Table 2) obtained by EPMA is in accordance with these observations. In fact, the Ti/Si chemical composition ratios are lower than what should be expected for a single Ti_5Si_3 phase. Moreover, the samples sintered at 1300 °C are depleted in Mg which explains the inexistence of XRD peaks of the Mg_2Si phase in all the samples sintered at this temperature. Some authors claim that the Mg_2Si phase decomposes at temperatures close to 620 °C, giving rise to MgO [18], which was not observed in the present work. Moreover, the magnesium oxide phase was not detected in this work, even after sintering at 1300 °C, probably because of the lower content of Mg in the final compacts. At this temperature the same phenomenon was observed for Cu and Ni. In both cases, the final contents of these elements are lower than the ones after sintering at 1100 °C or HIPing at

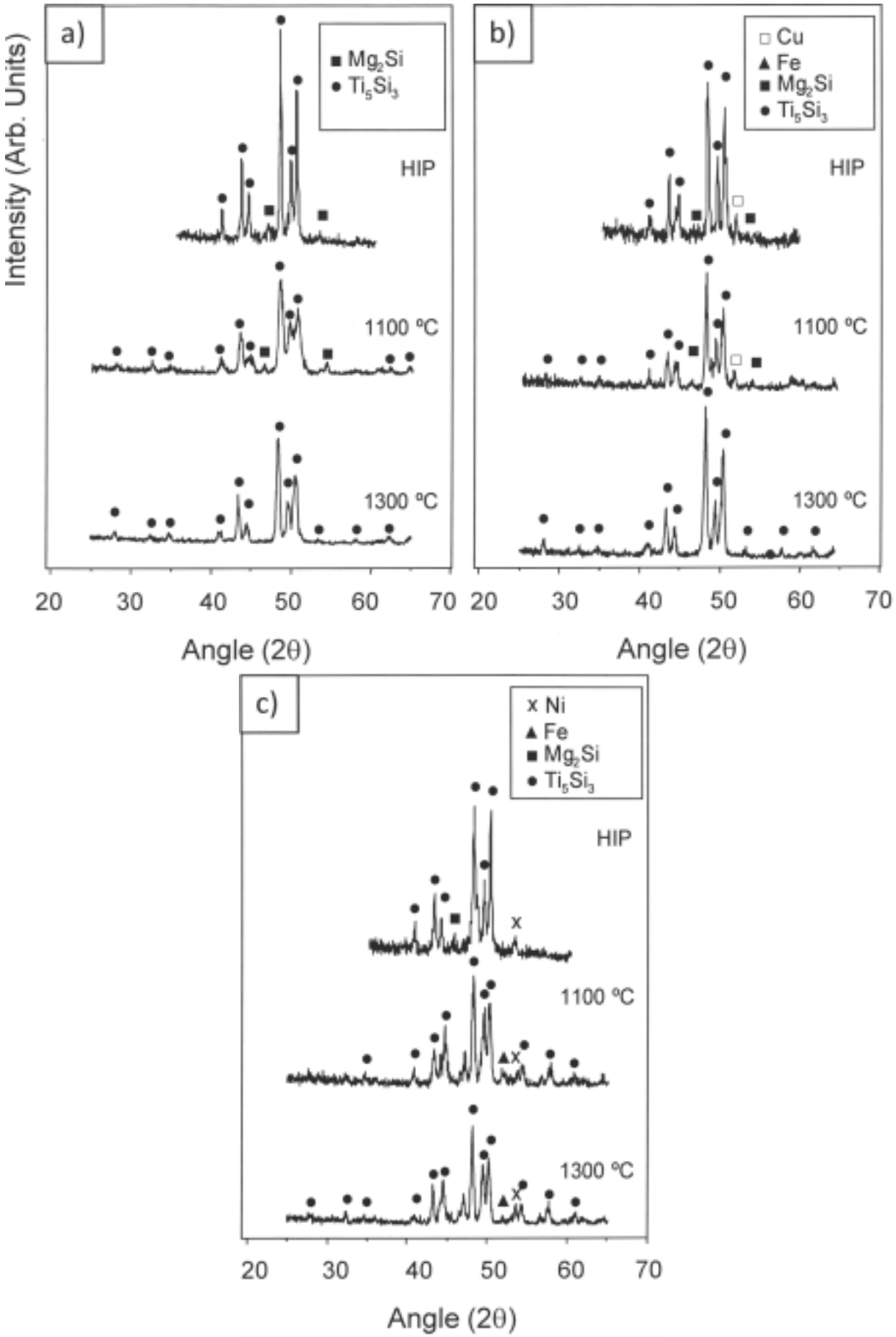

Fig. 6. XRD patterns of the uncoated (a), Cu-coated (b) and Ni-coated (c) Ti-35Si-10Mg samples sintered at two different temperatures and HIP'ed.

Table 3. Hardness and Young's modulus of the coated and uncoated Ti-35Si-10Mg samples sintered at two different temperatures and HIP'ed.

		Hardness (GPa)		*E*(GPa)
		4.9 N	0.245 N	
Ti-35Si-10Mg	1100 °C	4.1±0.4	10.2±0.3	-
	1300 °C	6.0±0.5	10.5±0.3	-
	HIP	6.9±0.2	10.3±0.3	191±15
Ti-35Si-10Mg+Cu	1100 °C	3.9±0.5	14.3±0.2	-
	1300 °C	7.2±0.2	14.1±0.2	-
	HIP	12.1±0.2	14.5±0.1	212±20
Ti-35Si-10Mg+Ni	1100 °C	4.3±0.3	15.2±0.3	-
	1300 °C	7.4±0.3	15.4±0.2	-
	HIP	13.0±0.2	15.0±0.3	210±17

Table 4.- Hardness of bulk Ti_5Si_3-based samples produced by different methods.

	Hardness (GPa)	Reference
Arc-melting	10-12	[1]
HIP of prealloyed powders	9-17	[2-7]
Modified hot pressing	11-13	[5]
Explosion synthesis	13	[9]
Electro discharge	14-15	[10]
Present work	10-15	-

900 °C. This means that the temperature of 1300 °C is too high for sintering of the theses samples since important changes of the chemical composition occurred. Moreover, the final densification of these samples is not so good (porosity values higher than 10%). Contrarily, the chemical composition of the HIP'ed samples is not so different from the one of the starting mixtures. Furthermore, good densification was achieved in the case of the coated particles, in particular for the sample with Cu coating. The role of Cu in promoting densification of Ti_5Si_3 has been confirmed in earlier works. According to Madan and German [19], the selection of the sintering aids of metal powders must take into account the mutual solubility of the matrix and the additive elements; the solubility limit of the additive in the matrix, and the relative magnitude of diffusivities of the additive and the matrix element at the grain boundary. According to these criteria, the figure of merit for sintering increases with decreasing solubility of the sintering aid in the matrix and with the increasing diffusivity of the matrix element in the second phase at the grain boundary. Hong *et al.* [20] calculated the figure of merits of various elements as individual sintering aids in Ti_5Si_3 and found that the value of Cu was the largest. Park et al. [16] obtained a high relative density of more than 99% for a Ti_5Si_3 + 6 wt.% Cu alloy sintered at a temperature of 1450 °C for 7 h.

3.4. Hardness and Young's modulus

Hardness and Young´s modulus results are shown in Table 3. Concerning hardness, the higher values were obtained for the HIP'ed coated samples as result of the better densification of these samples. Moreover, significant differences of hardness values were obtained for the two different loads. As expected, the higher the load the lower is the hardness. However, bigger differences were obtained for the samples with poor levels of densification. This is not a surprising result as for *F*=0.245 N, indentation in one single particle is possible and therefore, in this case, the influence of porosity on hardness is negligible. The ultramicrohardness values of the final compacts are in the range

10-15 GPa, the Ti-$_{35}$Si-$_{10}$Mg sample being the one with the lowest value. There are no structural reasons that might explain the higher hardness values of the coated samples. In fact, the Cu and Ni fcc phases are soft when compared to the intermetallic phases (Ti_5Si_3 and Mg_2Si). Consequently, the higher level of densification of the coated samples might, once again, be the reason for the higher hardness values obtained. The *H* values obtained in this work are slightly higher than the ones for arc-melted and cast alloy and are within the range of those of hot isostatically pressed and modified hot pressing from prealloyed powders (Table 4).

The values of *E* determined for the final compacts show the same trend as hardness, i.e the higher the densification level the higher the Young's modulus. However, within the standard deviation, the *E* average values obtained are almost identical, varying from 191 to 212 GPa. These values are higher than the ones reported in the literature for monolithic Ti_5Si_3 compound [16,21]. Using resonance frequency technique, Rosenkranz *et al.* [2] obtained a value of 160 GPa for a sample prepared by reaction sintering in vacuum. Kumar [21] reported a value of 150 GPa for the Ti_5Si_3 compound.

4. CONCLUSIONS

The influence of Ni and Cu intermediate layers on the sinterability of a surface modified Ti_5Si_3-based alloy synthesized by Mechanical Alloying was studied and the following conclusions were made:

1. A $(Ti,Mg)_5Si_3$ phase was formed during mechanical alloying of elemental Ti, Si, and Mg particles.
2. The deposition of Cu and Ni thin layers on the surface of the mechanically alloyed particles was possible by magnetron sputtering.
3. Beneficial effects of Cu and Ni coatings as sintering aids of the mechanically alloyed Ti_5Si_3 particles were observed.
4. The higher values of hardness and Young's modulus were obtained for the HIP'ed coated samples, as result of their better densification.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from Portuguese Foundation for Science and Technology (FCT) thought project POCI/CTM/57536/2004.

REFERENCES

[1] Y. Murata, T. Higuchi, Y. Takeda, M. Morinaga and N. Yukawa, In: *Proceedings of the International Symposium of Intermetallic Compounds, JIMIS-6*, ed. By O. Izumi (Sendai, Japan, 1991), p. 627.

[2] R. Rosenkranz, G. Frommeyer and W. Smarsly // *Mater. Sci. Eng. A* **152** (1992) 288.

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

[4] F. Simoes, N. Duarte and B. Trindade // *Rev. Adv. Mat. Sci.* **18** (2008) 293.

[5] K.S. Min, A.J. Ardell, S.J. Eck and F.C. Chen // *J. Mater. Sci.* **30** (1995) 5479.

[6] A.J. Thom, M.K. Meyer, Y. Kim and M. Akinc, In: *Processing and Fabrication of Advanced Materials III*, ed. by V.A. Ravi, T.S. Srivatsan and J.J. Moore (TMS, Warrendale, PA, 1994), p. 413.

[7] G. Frommeyer and R. Rosenkranz, In: *Int. Conf. On PM Aerospace Materials*, (MPR Publishing Services Ltd., Bellstone, Shrewsbury, U.K., 1991), p. 29:1.

[8] Hyung Chul Park, M.S. Kim and S.K. Hwang // *Scripta Materialia* **39** (1998) 1585.

[9] B.Y. Kang, H.S. Ryoo, W. Hwang, S.K. Hwang and S.W. Kim // *Mater. Sci. Eng. A* **270** (1999) 330.

[10] Y.W. Cheon, Y.J. Jo, C.M. Lee, H.S. Jang, K.B. Kim and W.H. Lee // *Mater. Sci. Eng. A* **467** (2007) 89.

[11] C.S. Byun, S. Bopark, D.K. Kim, W. Lee, C.Y. Hyun and P.J. Reucroft // *J. Mater. Sci.* **36** (2001) 363.

[12] J.M. Antunes, A. Cavaleiro, L.F. Menezes, M.I. Simoes and J.V. Fernandes // *Surf. Coat. Technol.* **149** (2002) 27.

[13] PDF#78-1429, *PDFWIN – International Centre for Diffraction Data*.

[14] PDF#85-1326, *PDFWIN – International Centre for Diffraction Data*.

[15] PDF#04-0850, *PDFWIN – International Centre for Diffraction Data*.

[16] K. J. Park, J. K Hong and S. K. Hwang // *Metall. Trans. A.* **28A** (1997) 223.

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

[18] M. Cavusoglu, O.N. Senkov and F.H. Froes // *Key Engineering Materials* **188** (2000) 1.

[19] D. S. Madan and R. M. German // *Powder Metall.* **33** (1990) 45.

[20] C. K. Hong and S. K. Hwang, In: *Proceedings of the 4th Powder Metallurgy*, (Korean Institute of Metals and Materials, 1992), p. 79.

[21] Y. Murata, T. Higuchi, Y. Takeda, M. Morinaga and N. Yukawa, In:

Proceedings of the International Symposium of Intermetallic Compounds, JIMIS-6, ed. by O. Izumi (Japan, 1991), p. 627.
[22] A. J. Thom, Y. M. Kim and M. Akinc // *Proc. Mater. Res. Soc. Symp.* **288** (1992) p. 1037.
[23] K.S. Kumar, In: *Intermettalic Compounds: Principles and Practice Vol. II*, ed. by J.H. Westtbrook and R.L. Fleischer (John Wiley & Sons, England, 1995), p. 211.