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Production of titanium matrix composites reinforced with SiC particles

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ABSTRACT

Titanium alloys exhibit high specific strength and stiffness that fit structural applications demanding lightweight construction. Ceramic reinforcements can improve specific strength and stiffness, and also the wear resistance. Higher specific strength and Young's modulus is expected when reinforcing titanium by SiC particles compared to other reinforcements. The production of a SiC reinforced titanium alloy using conventional powder metallurgy methods (PM) yields porosity and silicides formation. PM processing methods are discussed in this work: equal channel angular pressing, Spark plasma sintering, sintering using an induction oven and hot extrusion. Consolidation time and temperature are considerably decreased avoiding the silicide formation, while consolidation loads were increased to obtain a denser Ti–SiC composite. Hot extruded samples show the best results, without any reaction zone and a density near to the theoretical one.

1. Introduction

The thermo-mechanical and tribological properties of titanium alloys can be improved by reinforcing them with ceramics [1]. Continuous monofilaments like SiC improve considerably the strength of titanium alloys, especially at high temperatures, in the direction of the monofilaments [2]. Although Si reacts with titanium producing some brittle silicide phases, forming TiC_x and $Ti_5Si_3C_x$ [3], SiC monofilaments are nowadays widely used as reinforcement of Ti alloys and Ti aluminide matrices [4]. Other previous works studied the development of such reaction layers and their properties as well as the influence of the alloying elements, the parameters of production, and the possibility of protective coatings on the SiC reinforcement [5–7]. The reactions between metal matrices and ceramic particles not always imply a degradation of the mechanical properties. For example, in the case of AlMgSi reinforced with Al_2O_3 particles spinel reaction occurs at the particle/matrix interface, which does not degrade the MMC properties [8]. In general, the continuous reinforced metal matrix composites present high specific strength and stiffness in the direction of the fibres, and normally they are costly, non formable and difficult for machining. If a more or less isotropic material is needed, and/or if the hot forming, machinability is also needed, the particulate reinforced titanium matrix composites (PRTi) are a better choice, normally at lower prices. The particles investigated in previous works as reinforcement of titanium alloys are ceramics: TiC [9], TiN [10], TiO_2 [11], Si_3N_4 [12], SiC [13], TiB_2, TiB [14,15], oxides: Al_3O_2 (in titanium aluminides [16]), Zr_2O_3, R_2O_3 (with R = rare element) [17,18], and intermetallic compounds: Ti_3Al or TiAl [19] and Ti_5Si_3 [20].

SiC particles promise a stronger increase of the specific Young's modulus, but the SiC particle reinforced titanium alloys produced by conventional powder metallurgy tend to be porous and present a brittle interface reaction zone [21]. The objective of this work is to find a method to produce titanium reinforced with SiC particles with low porosity and with as little amount as possible of silicides by using different processing methods where time and/or temperature are reduced.

2. Experimental procedures

The consolidation methods of powders are described in Fig. 1 and Tables 1 and 2.

ECAP: Severe plastic deformation methods such as equal channel angular pressing (ECAP) have been used in the last years to obtain fine grained structures in alloys by imposing high levels of strains [22–24]. The consolidation of powders using ECAP can be done at low temperatures, because the large shear deformation involved in this process is able to break the surface oxide layer and create good contact between particles. Bonding is achieved instantaneously as the particles pass the shearing zone, in contrast to normal sintering which requires a long time for diffusion [25].

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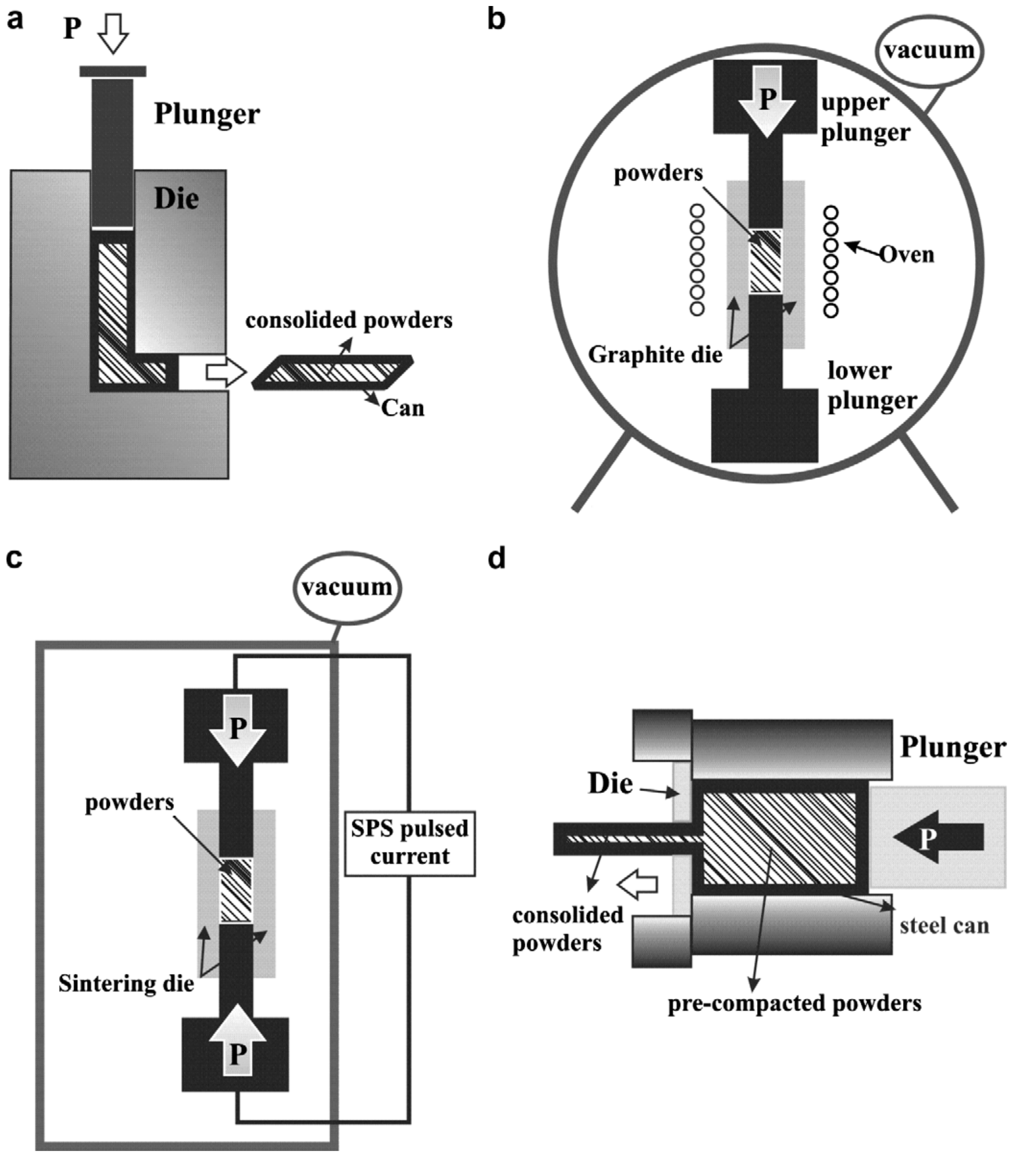

Fig. 1. Powder metallurgy methods to produce titanium reinforced with SiC particles, (a) ECAP, (b) compressive inductive heated, (c) spark plasma sintering and (d) hot extrusion.

Table 1
First trial on producing Ti64/SiCp composite by hot pressing

Sample	Powders Ti64	%SiC/ size	Holding time (min)	Temperature of HIP (°C)	Rate of compression (kN/min)
S01	Round dry mixed	20/F600	30	1000	8
S02	Round dry mixed	20/F600	5	1000	8
S03	Round dry mixed	20/F400	15	900	4
S04	Round dry mixed	20/F400	5	850	8
S05	Round dry mixed	20/F400	5	880	4
S06	Round dry mixed	20/F400	60	880	4
S07	Round dry mixed	15/F400	60	910	4
S08	Irregular dry mixed	15/F400	15	900	4
S09	Irregular wet mixed	15/F400	15	900	4

Table 2
Test parameters to produce Ti reinforced with SiC particle

Sample	%SiC	Method	Holding time	Temperature (°C)	Observations
ECAP01	5	ECAP	15 min	250	Copper can
ECAP02	5		15 min	300	Copper can
ECAP03	15		15 min	300	Steel can
IND01	15	Compressive	30 s	800	
IND02	15	induction heated	30 s	900	
IND 03	15		5 min	800	
IND 04	15		10 min	850	
IND 05	15		5 min	900	
Spark	15	SPS	0–5 min	700–1000	
HE01	15	Hot extrusion	15 min	800	Not successful
HE02	8		15 min	850	
HE03	8		15 min	900	
HE04	15		15 min	950	

Compressive induction heating: This process is based on the high heating rates achieved by an induction furnace, and the high uniaxial compression pressure up to 50 MPa imposed to the powder mixtures.

Spark plasma sintering (*SPS*): It can be roughly compared with the conventional hot pressing technology. High density current pulses (several thousand kA with a pulse length of about 3–5 ms) at low voltage (less than 50 V) are applied directly to the powder and the pressing tool. It is supposed that the On–Off-DC pulses in the early stage of this process generate a spark discharge followed by rapid Joule heating due to the high resistivity between the particles of the powder. The fast local increase of temperature assisted by pressure promotes the elimination of adsorbed gas and breaks the surface oxide layers of powders [27]. SPS offers advantages such as rapid heating rate (e.g. up to 600 °C/min) and short holding time compared to conventional HP or HIP.

Hot extrusion: Extrusion produces compressive and shear forces in the stock. The shear stresses create higher deformations, i.e. break oxide layers to consolidate the powders. This method was used as a secondary process, for example, to refine the matrix grains or to achieve a better particle distribution in metal matrix composites. Nowadays the hot extrusion is used to consolidate powders after cold pressing [26,27].

Rounded Ti64 powders and irregular SiC powders were used for conventional hot pressing and for the SPS trials. The other methods were carried out using pure round Ti powders and irregular SiC powders mixed in a mortar in an Ar atmosphere. Irregular size distribution of the pure Ti powders and the SiC particles can be observed in Fig. 2. SiC volume fractions of 5%, 8%, 15% and 20% were used. The consolidated samples were observed by light optical microscopy (LOM) and scanning electron microscopy (SEM). EDX was used to study the interface between the matrix and the particles. Relative density was measured using the Archimedes method.

2.1. Conventional hot pressing

Powders of Ti-6Al-4V round or edged were dry or wet mixed with SiC particles. The mixture was put in a graphite die, heated up to the sintering temperature in argon atmosphere between 880 and 1000 °C at about 10 K/min, held at this temperature, and cooled down at about 10 K/min. During the whole process, the pressure was held at 40 MPa. Table 1 shows the parameters used for these trials.

2.2. ECAP

Two cans of pure copper and one of steel (low carbon annealed) were filled with the powder mixture. Composite materials with 5vol% and 15vol% particles were produced. In the first two cases, powder was compacted in loose form. In the third case, encapsulated and degassed mixture powder was cold isostatic pressed at the pressure of 1 GPa. Canned samples were inserted into the ECAP die preheated to the consolidation temperature (250 and 300 °C) and warmed for 15 min. Average ram speed during consolidation was 3 mm s^{-1}. Inlet and outlet channels of ECAP tool had the length of 110 mm and the channel intersection angle $\Phi = 90°$ with outer radius angle $\Psi = 0°$, give an equivalent strain of 1.15 during consolidation. The cross-section of both rectangular channels was 12 × 12 mm. A Cu or steel block was inserted into the channel in front of the container to increase hydrostatic pressure during pressing and the lubricant used was a solution of colloidal graphite.

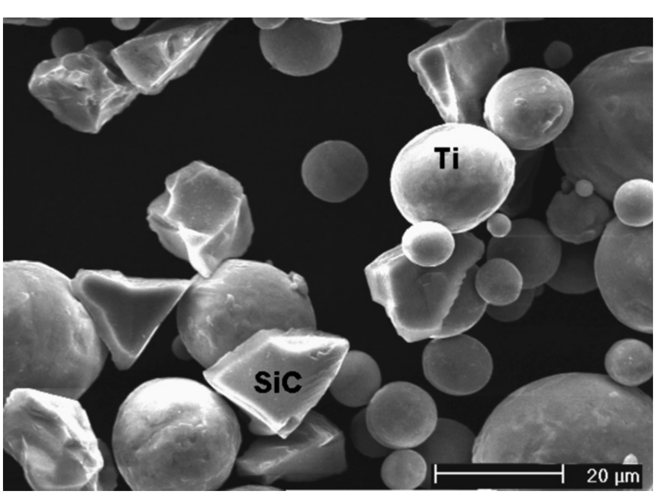

Fig. 2. Ti (round) and SiC (blocky) powder mixture before consolidation.

2.3. Compressive induction heating

The mixed powders were put inside a graphite die of 10 mm of diameter and closed inside the chamber with the upper and lower plungers. The chamber was degassed and the powders were uniaxial cold compacted. The compaction achieved by the uniaxial compression is low. During compression, the die was heated up to the consolidation temperature at a heating rate of 10 K/s, and held to this temperature during holding times from 30 s to 10 min. This process was carried out at high temperatures during short times.

2.4. Spark plasma sintering (SPS)

The Ti64/SiC powder mixture was heated stepwise up to temperatures between 800 °C and 1100 °C for the spark plasma process. The heating rate was about 100 K/min. The sintering was done with holding times between 0 and 5 min. The specific characteristic of the SPS is the usage of a pulsed electric current for the direct heating of the pressing tool and the sample by the generation of Joule heat. This feature can lead to temperature differences between the die and the sample depending on the material conductivities and on the processing conditions (heating rate, tool geometry). Representative parts of the sintered discs were analysed to measure local properties and the overall homogeneity.

2.5. Hot extrusion

Steel cans of 40 mm of diameter and 60 mm of length were filled with the mixture of powders, degassed and gas-proof sealed. The cans were heated up to the test temperature during 15 min in a furnace under argon atmosphere, and the die was heated to 400 °C. The samples were hot extruded during short periods of time and at 10 mm/s. To achieve the shear stresses, the ratio of extrusion was 1:16.

3. Results and discussion

3.1. Conventional hot pressing

This method produced only samples with high porosity and large reaction zones (2–20 µm) for all the tested parameters. Fig. 3a shows the sample reinforced with 20% of F600 SiC particles, produced at 1000 °C during 30 min. The SiC particles were almost completely consumed by the reaction with Ti. If the holding time is reduced to 5 min, the reaction zone is smaller (Fig. 3b), but high porosity is observed due to incomplete sintering. Furthermore, cracks can be observed in the brittle reaction zone. The best results were observed at 900 °C and 15 min (Fig. 4a). EDX line-scan test shows that Si and Ti form the reaction layer zone (Fig. 4b)

3.2. Improved methods

The results of all the other processing methods are summarized in Table 3.

The load used to consolidate the ECAP samples was measured during the movement of the ram. A pressure up to 800 MPa was reached at 250 °C, whereas a pressure of 550 MPa was needed at

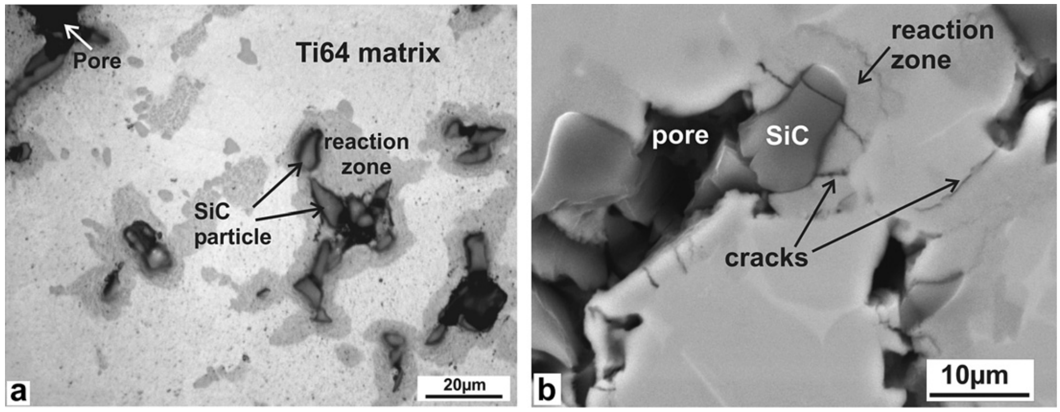

Fig. 3. Samples produced by conventional hot pressing using uniaxial compression. (a) 20% of F600 SiC particles, temperature 1000 °C and holding time of 30 min showing the particles of SiC almost totally consumed, (b) 20% of F600 SiC particles, temperature 1000 °C and holding time of 5 min showing the brittle reaction layer and the non-sintered titanium powders.

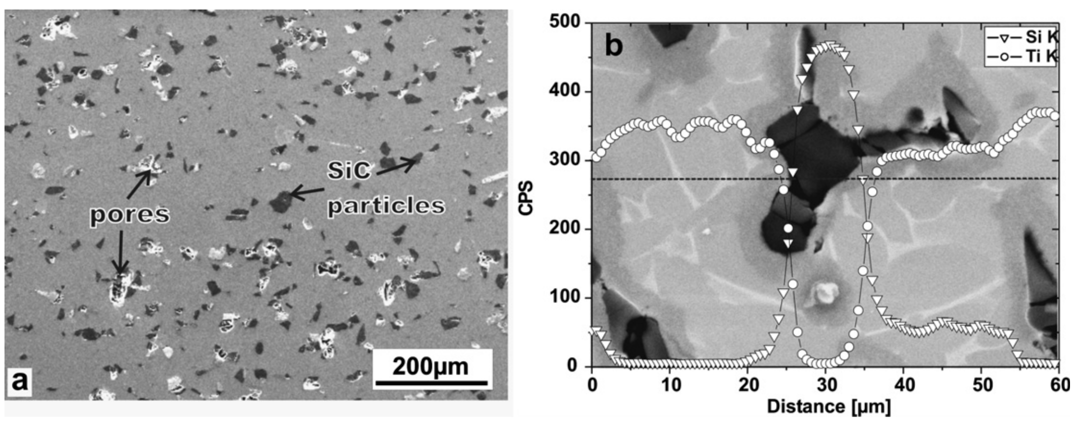

Fig. 4. (a) 15 vol% of F400 SiC particles, produced at 910 °C and holding time 60 min showing a small reaction layer and residual porosity, (b) EDX line-scan showing the distribution of Ti and Si across the dashed line, showing both Ti and Si in the reaction zone. Light grey: beta phase, grey: alpha phase, dark grey: reaction zone and black: SiC particles.

Table 3
Summary of the results

Sample	Results
ECAP01 ECAP02 ECAP03	Macro-cracks; micro-cracks at the ceramic particles
IND01 IND02	Ti powders not sintered; non reaction layer
IND 03 IND 04 IND 05	Ti powders almost sintered; non reaction layer Porosity at the SiC clusters due to incorrect mixture of the powders
SPARK	The gradient of temperature provoked zones with porosity and zones with reaction zones
HE01 HE02 HE03 HE04	Powders not extruded owing to insufficient force No cracks, non reaction layer

a temperature of 300 °C. The ECAP samples were not completely compacted, as shown in Fig. 5. Inside the can the powders are distributed into dense composite zones, separated by cracks of many millimetres. Dense zones are shown in Fig. 5a and b; neither reaction zone, nor porosity are observed. If low back-pressure is applied, no hydrostatic stresses are developed, which are needed for consolidation. That is the reason why the cracks are formed during ECAP consolidation. Insufficient amount of back-pressure during consolidation resulted in formation of macro cracks parallel to shearing plane within compacted powders. Cold pre-compaction and steel can (higher back pressure), showed better results than the powders consolidated in the copper can.

The samples produced by compressive induction heating do not show any reaction zone. Fig. 6a shows some porosity due to the low temperatures and/or short holding times that are not enough to sinter the titanium powders. By increasing the holding time (10 min at 850 °C), less porosity was expected, but the inhomogeneous SiC particle distribution in this case resulted in clusters where no sintering occurred (Fig. 6b). Fig. 7 shows the plunger displacement with the time. The major densification occurs while heating the sample under compression. The lower densification of the sample produced at 850 °C during 10 min agree with the porous microstructure observed. During the holding time at high temperatures, sintering (diffusive process) occurs, and the microporosity disappears by slower densification rate.

The hot extruded samples showed the best results (lowest porosity and no reaction zone) at temperatures between 850 and 950 °C. At 800 °C no consolidation was achieved, because the force needed was higher than the maximal force provided by the ma-

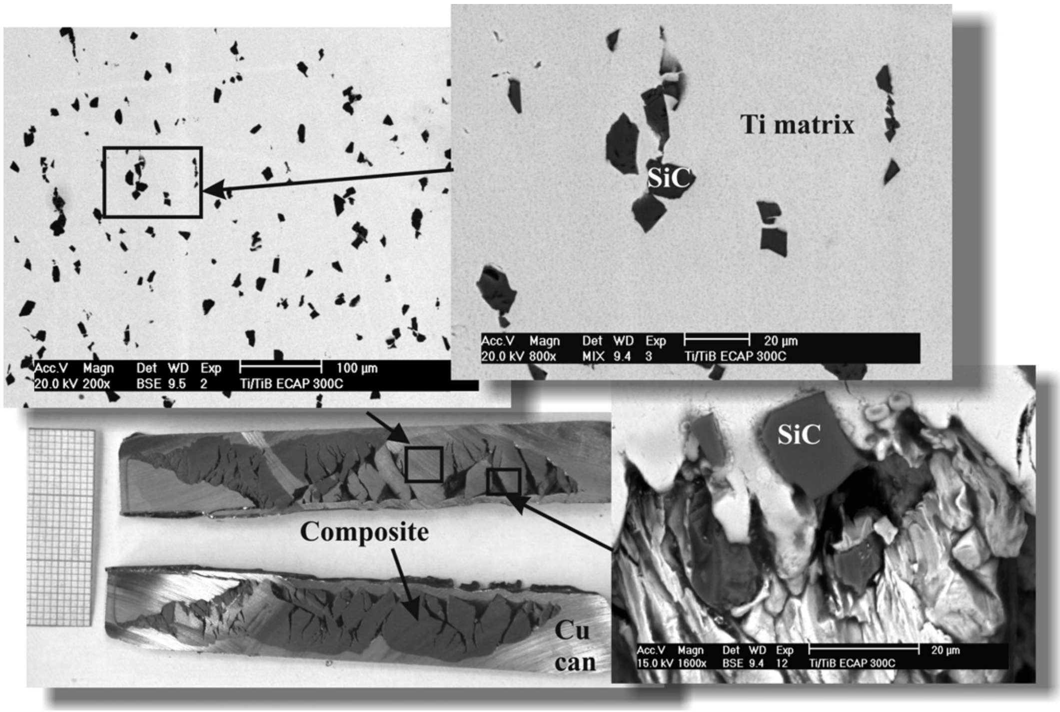

Fig. 5. ECAP sample produced at 300 °C inside the copper can, showing the macro-pores, and the compacted parts with few micro-cracks and without a reaction layer.

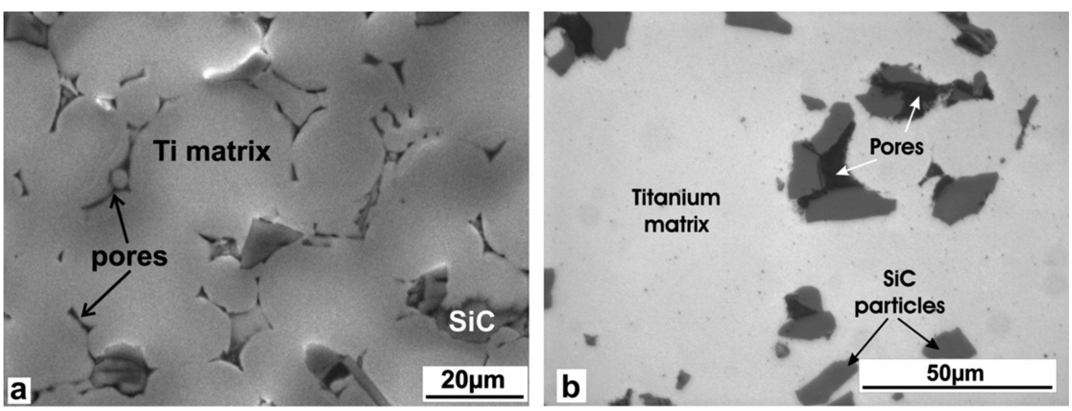

Fig. 6. Samples produced by compressive induction heating (a) at 800 °C during 30 s of holding time showing incompletely sintered Ti powders, (b) at 850 °C during 10 min, showing sintered powders, but porosity at the SiC particle clusters formed during the mixing.

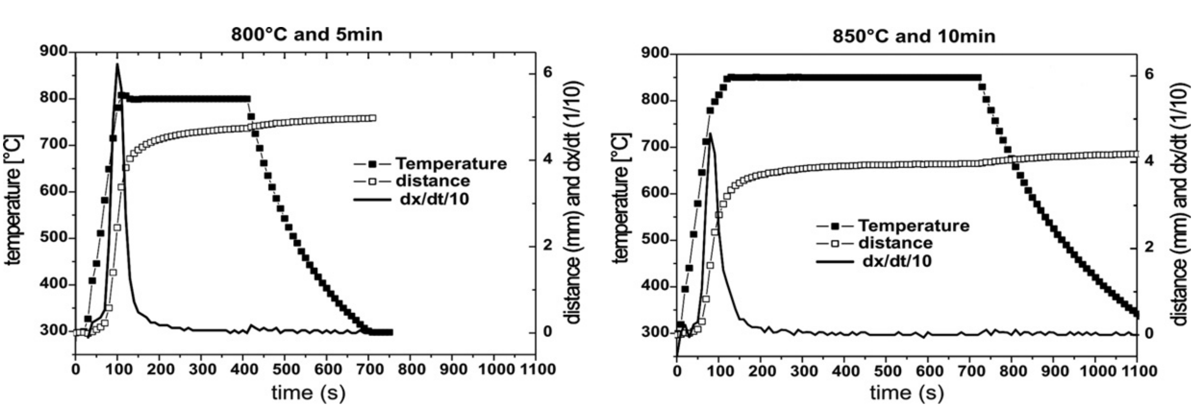

Fig. 7. Temperature, plunger displacement (x) and dx/dt as a function of time for consolidation by compressive inductive heated at (a) 800 °C during 5 min, and (b) 850 °C during 10 min showing the maximal compression rate during heating and less compression for the material consolidated at 850 °C and 10 min.

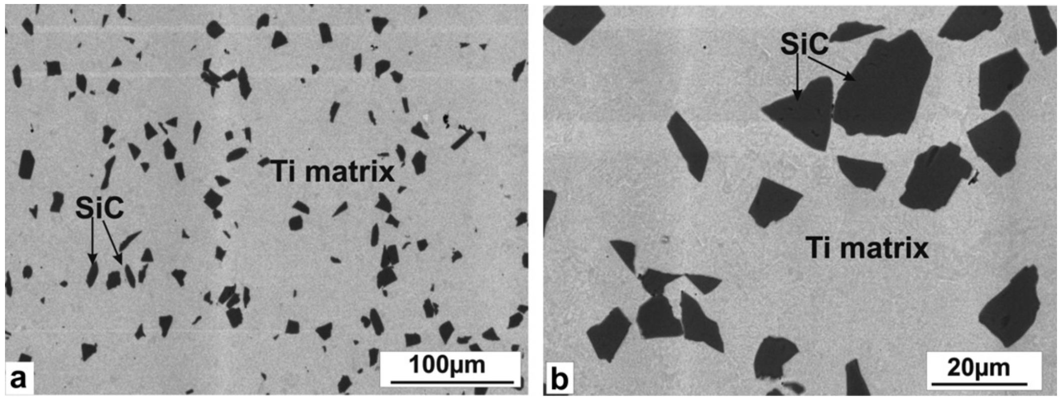

Fig. 8. Composite produced by hot extrusion at (a) 850 and (b) 950 °C, respectively, showing no cracks, no pores and no reaction zone.

chine. Fig. 8 shows the hot extruded materials at (a) 850 °C and (b) 950 °C. No reaction zone and low porosity inside the SiC clusters were found, and a slight alignment of the SiC particles in the direction of the extrusion was observed.

In Figs. 9 and 10 the relative densities are indicated. The density of the ECAP sample is taken from the compacted zone. The sintered samples show relative densities values under 98%, except for the sample S107, sintered at 910 °C during 60 min, where the relative density almost reaches the theoretical one. The hot extrusion samples show densities near 100% of the theoretical one, and almost no differences in the range of temperatures of hot extrusion. The samples produced in the inductive furnace show relative densities up to 99%. The increase in the volume fraction of SiC particles provokes clustering of the ceramics, and with this, some porosity, shown in the sample heated at 850 and 900 °C and held for 10 and 5 min, respectively, as seen in Fig. 6.

The density of the SPS samples increases with increasing sintering temperature. Compared with the conventional hot pressing,

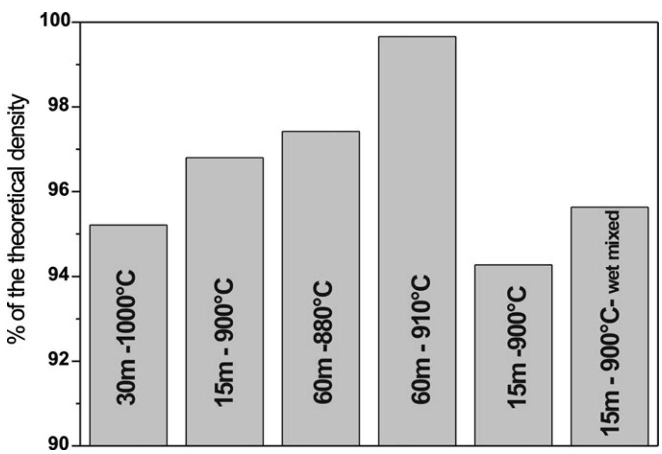

Fig. 9. Percentage of the theoretical density for the sintered samples.

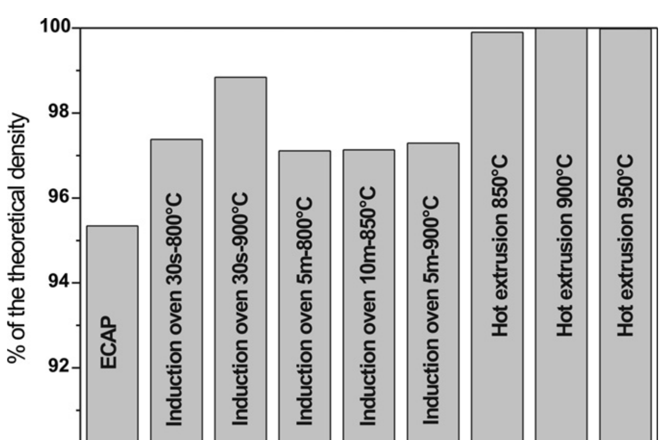

Fig. 10. Percentage of the theoretical density for the composite production methods (ECAP porosity measured in the compact zones).

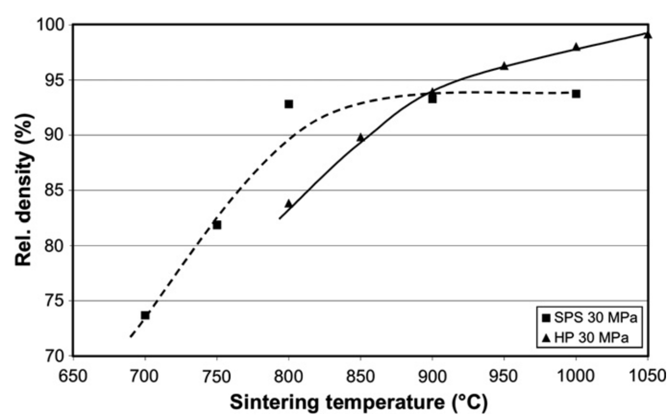

Fig. 11. Relative density with the sintering temperature showing higher density with the spark plasma method (SPS) compared to the conventional sintering, hot pressing (HP) at lower temperature.

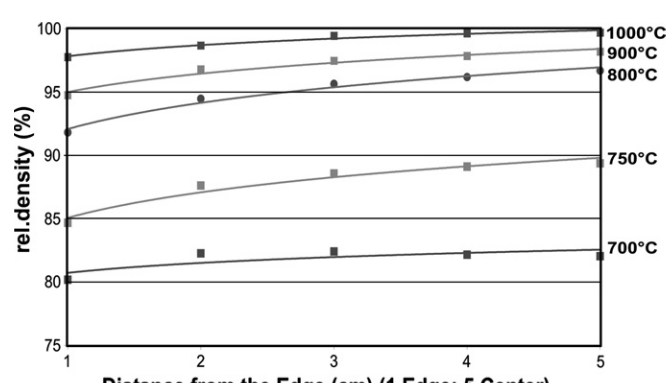

Fig. 12. Relative density in the SPS sample with the distance from the edge at different temperatures of consolidation.

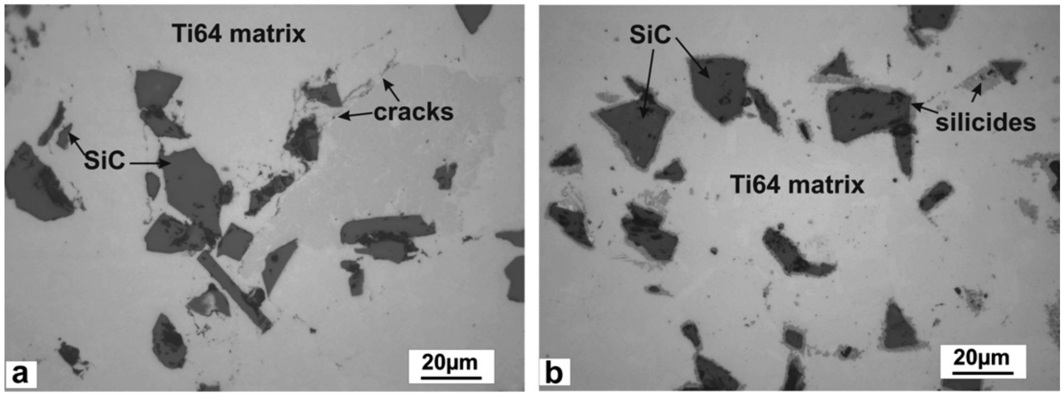

Fig. 13. Microstructures of SiC reinforced titanium produced by the spark plasma, showing (a) porosity at the edge, and (b) reaction layer in the middle of the ingot.

the maximum density stagnates at lower values (Fig. 11). The higher density at lower temperatures can be explained with the differences in temperature measurement. A sintering temperature of at least 800 °C is necessary for densification. This value corresponds to the average density of the whole sintered sample. The samples show higher densities at the centre of the cylindrical disc compared to the outside margin with a 3–5% higher porosity (Fig. 12). In addition, reaction layers between the reinforcement and the titanium matrix can be revealed only near the centre (Fig. 13). These results provide evidence for a temperature difference more than 100 °C across the 100 mm diameter sample during SPS. More effective thermal insulation of the pressing tools leads to a more homogeneous density distribution. This technique can be used for sample diameter up to 100 mm. Up to now, the complete densification of SiC-particulate reinforced Titanium-alloy based composites by spark plasma sintering without reactions between reinforcement and matrix is only shown for small samples (diameter less than 15 mm) [28].

4. Conclusions

Long times of consolidation at high temperatures not only achieve the sintering of the titanium powders but also promote the formation of silicides by dissolution of SiC particles.

Titanium reinforced with SiC particles composites of good quality were produced using hot extrusion at 850–950 °C, with densities near 100% the theoretical one, no reaction zone and a good particle distribution slightly oriented in the extrusion direction. The pre-heating time in the furnace under Ar atmosphere before hot extrusion was about 15 min.

The combination of shear and compression strains, and the pre-heating of the sample near the beta transus temperature results in a good compaction.

Large shear strains alone, without the combination of compression, like in ECAP consolidation, are not enough for the densification of the powders.

The SPS technology is not applicable for large samples because of the temperature gradient that produces a gradient of porosity and reaction zones across the material.

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References

[1] Poletti C, Merstallinger A, Schubert T, Marketz W, Degischer HP. Materialwissenschaft und Werkstofftechnik 2004;35:741–9.
[2] Peters M, Leyens C. Titan und titanlegierungen. Weinheim: Wiley VCH; 2002.
[3] Gorsse S, Le Petitcorps Y. Compos A 1998;29A:1221–7.
[4] Djanarthany Sarala, Viala Jean-Claude, Bouix Jean. Mater Sci Eng A 2001;300(1–2):211–8.
[5] Shatwell RA. Mater Sci Eng A 1999;259:162–70.
[6] Mogilevsky P, Werner A, Dudek HJ. Mater Sci Eng A 1998;242(1–2):235–47.
[7] Quenisset JM, Fromentin JF, Le Peticorps Y, Debray K, Martin E. Compos Sci Technol 1996;56(7):767–75.
[8] Requena G, Telfser D, Hörist C, Degischer HP. Mater Sci Technol 2002;18:515.
[9] Kim YJ, Chung H, Kang SJL. Mater Sci Eng A 2002;333(1–2):343–50.
[10] Cui ZD, Zhu SL, Man HC, Yang XJ. Surf Coatings Technol 2005;190:309–13.
[11] Joshi PB, Marathe GR, Murti NSS, Kaushik VK, Ramakrishnan P. Mater Lett 2002;56:322–8.
[12] Alman DE, Hawk JA. Wear 1999;225–229:629.
[13] Selamat MS, Watson LM, Baker TN. J Mater Proc Technol 2003;142:725–37.
[14] Furuta T, Yamaguchi T, Shibata Y, Saito T. Titanium'99. In: Proceedings of the ninth world conference of titanium, 1999. p. 1917–24.
[15] Godfrey TMT, Goodwin PS, Ward-Close CM. Titanium'99. In: Proceedings of the ninth world conference of titanium, 1999. p. 1868–77.
[16] Lapin J, Ondrus̆ L, Bajana O. Mater Sci Eng A 2003;360:85–95.
[17] de Castro V, Leguey T, Muñoz A, Monge MA, Pareja R. Mater Sci Eng A 2006;422(1–2):189–97.
[18] Geng Ke, Lu Weijie, Yang Zhifeng, Zhang Di. Mater Lett 2003;57:4054–7.
[19] Zhanga E, Zenga S, Wang B. J Mater Proc Technol 2002;125–126:103–9.
[20] Clyne TW, Flower HM. Titanium'92, science and technology, 1993. p. 2467–78.
[21] Kooi BJ, Kabel M, Kloosterman AB, De Hosson JThM. Acta Mater 1999;47:3105–16.
[22] Stolyarov VV, Zhu YT, Alexandrov IV, Lowe TC, Valiev RZ. Mater Sci Eng A 2003;343(1–2):43–50.
[23] Shin DH, Park KT. Mater Sci Eng A 2005;410–411:299–302.
[24] Raab GJ, Valiev RZ, Lowe TC, Zhu YT. Mater Sci Eng A 2004;382(1–2):30–4.
[25] Xia K, Wu X. Scripta Mater 2005;53:225–1229.
[26] Salvador MD, Amigó V, Martinez N, Busquets DJ. J Mater Proc Technol 2003;143–144:605–11.
[27] Ukai S, Hatakeyama K, Mizuta S, Fujiwara M, Okuda T. J Nucl Mater 2002;307–311:758–62.
[28] J. Schmidt, T. Weissgaerber, T. Schubert, B. Kieback, Advances in Powder Metallurgy; Particulate Materials 2006; Proc. of the 2006 Int. Conference on Powder Metallurgy ; Particulate Materials, San Diego (USA); June 2006, Part 9, p. 85-94.