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Abstract

Titanium alloys exhibit high specific strength and stiffness that fit structural applications demanding lightweight. 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 considerable 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.

Keywords: Metal-matrix composites (MMCs); Interface; Extrusion; Powder processing; Sintering

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 aluminides 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, 6, 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 stress 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 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] 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 conventionally 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 Figure 1, Table 1 and Table 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, 23, 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].

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 50MPa 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 to 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 particles [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 oxides 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 was 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 rounded 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 Figure 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 rounded 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 10K/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 two different particle volume fractions were produced, with 5vol% and 15vol% respectively. In the two first cases, powder was compacted in loose form. In the third case, encapsulated and degassed mixture powder was cold isostatic pressed at the pressure of 1GPa. Canned samples were inserted into the ECAP die preheated to the consolidation temperature (250 and 300°C) and warmed for 15 minutes. Average ram speed during consolidation was 3mm.s^{-1}. Inlet and outlet channels of ECAP tool had the length of 110mm and the channel intersection angle Φ=90° with outer radius angle Ψ = 0°, give an equivalent strain of 1.15 during consolidation. The cross-section of both rectangular channels was 12 x 12mm. 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.

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 10K/s, and held to this temperature during holding times from 30s to 10m. 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 minutes 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 (2-20μm) for all the tested parameters. Figure 3a shows the sample reinforced with 20% of F600 SiC particles, produced at 1000°C during 30min. The SiC particles were almost completely consumed by the reaction with Ti. If the holding time is reduced to 5min, the reaction zone is smaller (Figure 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 minutes (Figure 4a). EDX line-scan test shows that Si and Ti form the reaction layer zone (Figure 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 a temperature of 300°C. The ECAP samples were not completely compacted, as shown in Figure 5. Inside the can the powders are distributed into dense composite zones, separated by cracks of many millimetres. Dense zones are shown in Figure 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 backpressure 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. Figure 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 minutes at 850°C), less porosity was expected, but the inhomogeneous SiC particle distribution in this case resulted in clusters where no sintering occurred (Figure 6 b). Figure 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 minutes agree with the porous microstructure observed. During the holding time at high temperatures, sintering (diffusive process) occurs, and the micro-porosity 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 machine. Figure 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 Figure 9 and Figure 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 minutes, 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 during 10 and 5 minutes respectively as seen in Figure 6.

The density of the SPS samples increases with increasing sintering temperature. Compared with the conventional hot pressing, the maximum density stagnates at lower values (Figure 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 (Figure 12). In addition, reaction layers between the reinforcement and the titanium matrix can be revealed only near the centre (Figure 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 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 minutes.

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.

5 Acknowledgments

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Tables

Figure captions

6 References.

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Figure 1

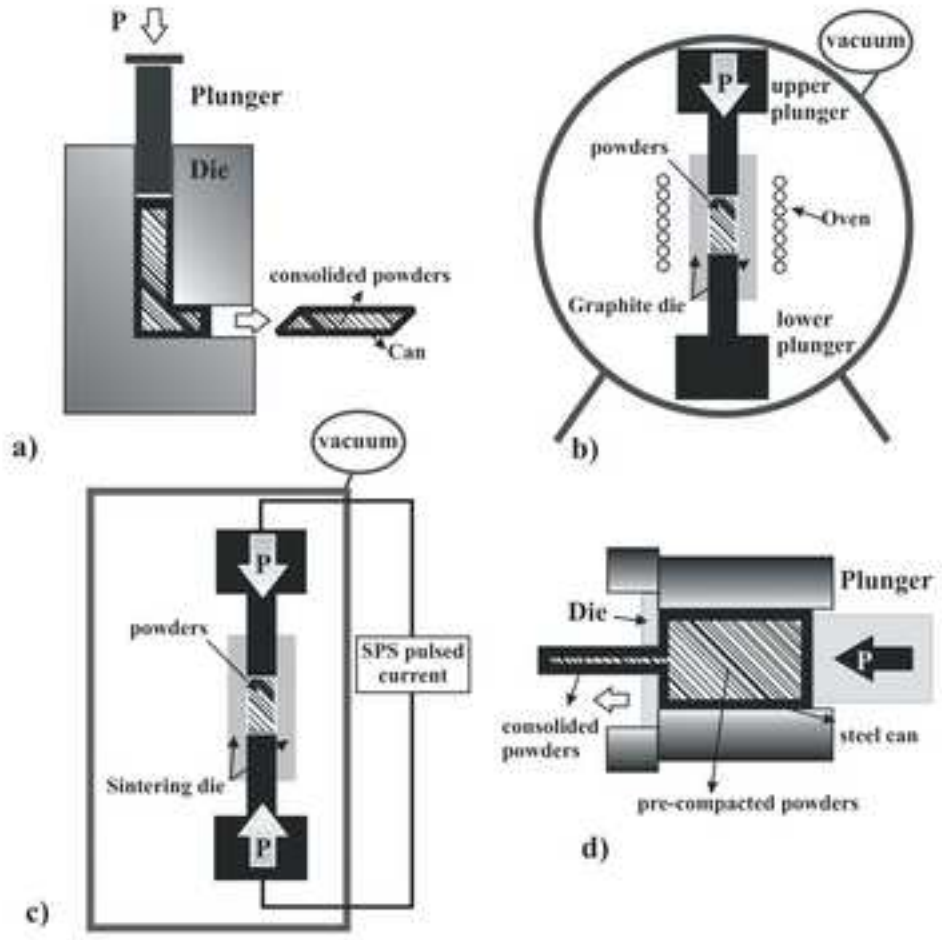


Figure 2

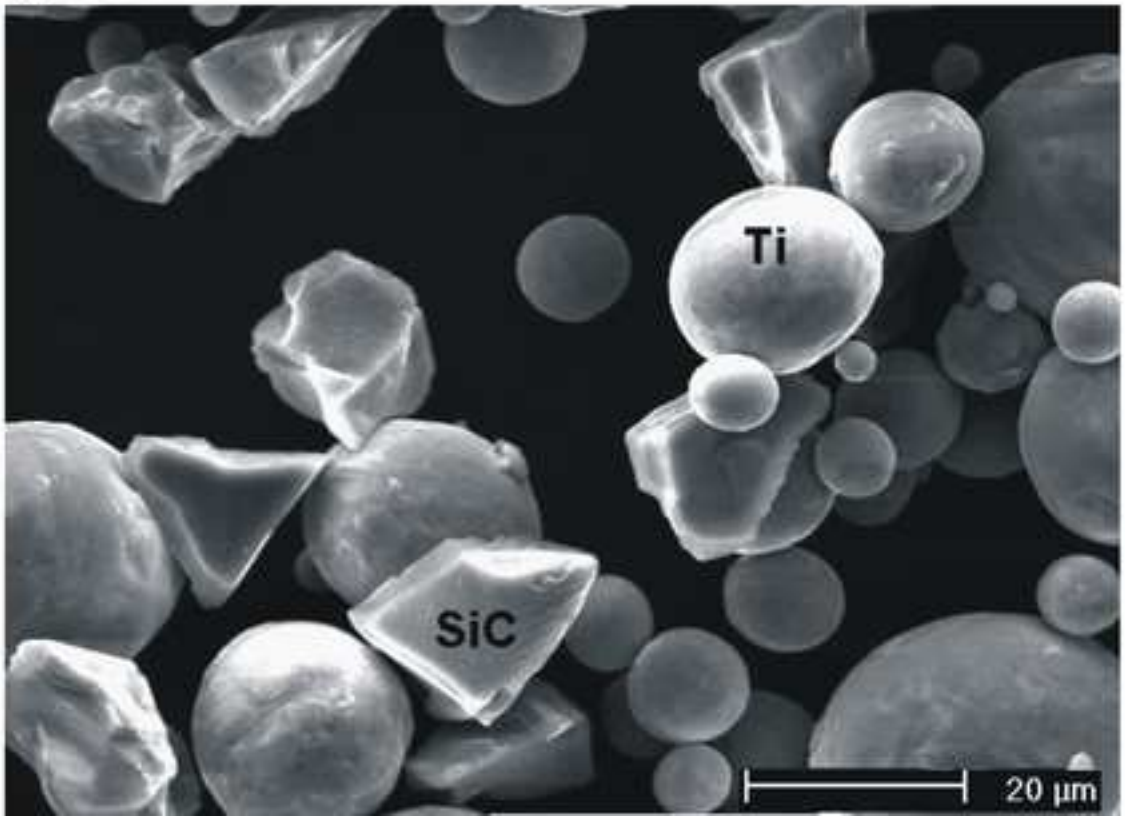


Figure 3

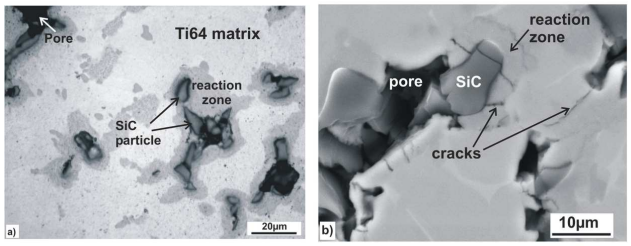


Figure 4

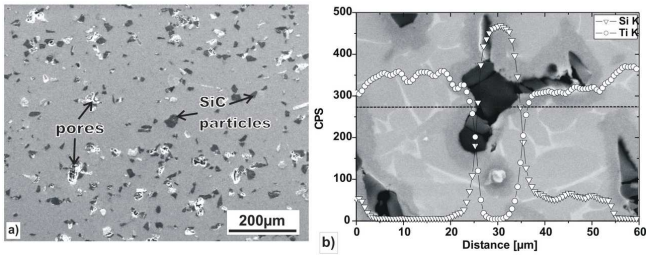


Figure 5

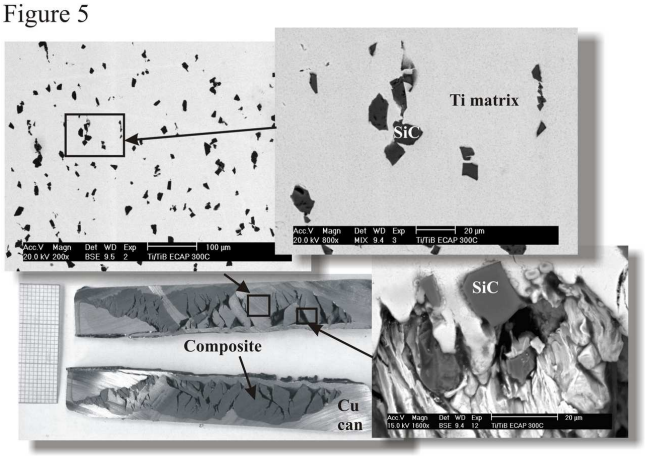
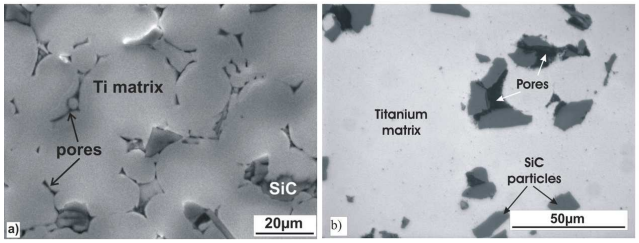


Figure 6



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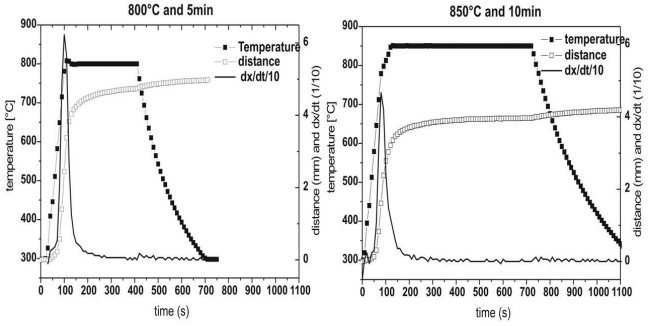
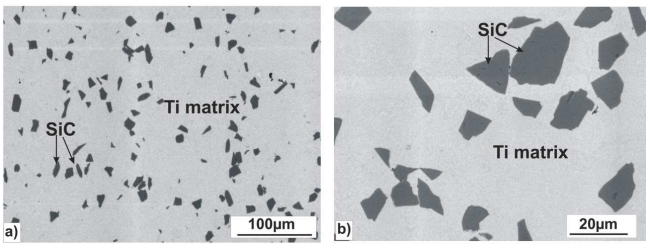


Figure 8



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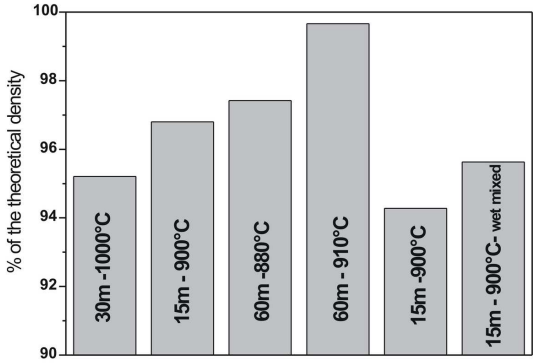


Figure 10

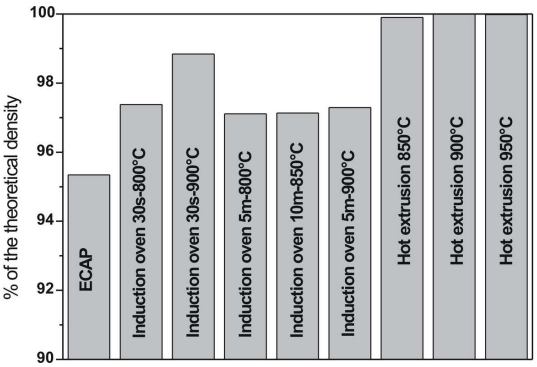
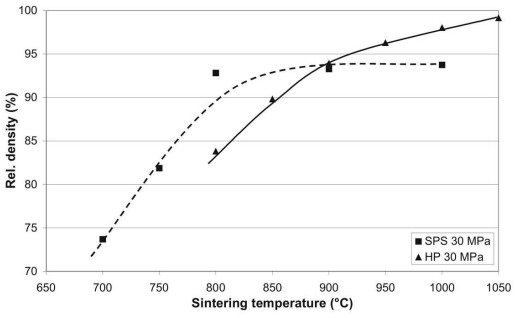


Figure 11



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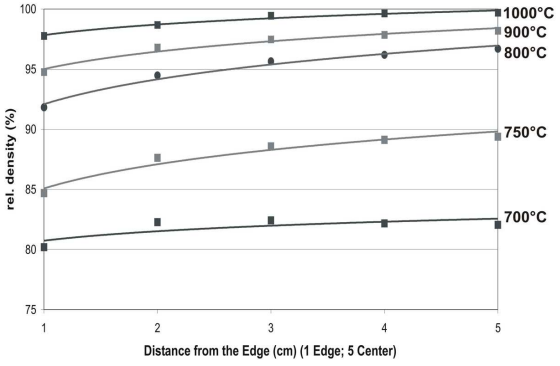

Figure 13

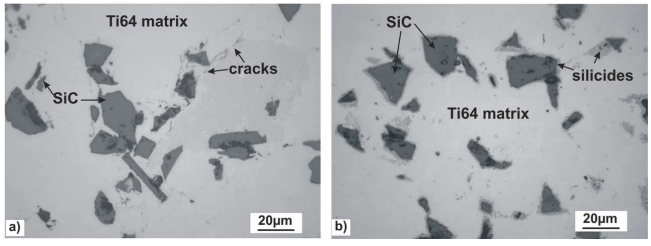

Table 1

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

Table 2

Sample	% SiC	Method	holding time	temperature	Observations
ECAP01	5	ECAP	15m	250°C	Copper can
ECAP02	5		15m	300°C	Copper can
ECAP03	15		15m	300°C	Steel can
IND01	15	Compressive Induction heated	30s	800°C	
IND02	15		30s	900°C	
IND 03	15		5m	800°C	
IND 04	15		10m	850°C	
IND 05	15		5m	900°C	
SPARK	15	SPS	0-5min	700-1000°C	
HE01	15	Hot extrusion	15 m	800°C	Not successful
HE02	8		15 m	850°C	
HE03	8		15 m	900°C	
HE04	15		15 m	950°C	

Table 3

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