Production of γ-TiAl based alloy by combustion synthesis + compaction route, characterization and application

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Abstract

Synthesis and densification of γ-TiAl alloy with nominal chemical composition Ti-48Al-2Cr-2Nb (at.%) have been investigated. The alloy is prepared in one step using a combustion synthesis + compaction process, where the synthesis and the shaping take place at the same time. Two different combustion routes are used: Forced Self-propagating High-temperature Synthesis + Compaction (FSHS + C) and Thermal Explosion + Compaction (TE + C). The optimal synthesis parameters such as ignition point, load application delay time, load value, load holding time, heating and cooling rates are determined. After the processing, the density of the samples was measured to be of about 99 % of the theoretical value. It is shown that the oxygen content can be controlled during the processing and products with the same or lower oxygen content than that in the original raw material can be obtained. Analysis of chemical composition and microstructure shows that a complete chemical homogenization, required phase composition, desired lamellar microstructure and relaxation of possible internal stresses require additional thermal treatment of samples prepared by both FSHS + C and TE + C processes.

Key words: self-propagating high-temperature synthesis (SHS), combustion synthesis, intermetallics, titanium aluminides, TiAl

1. Introduction

In recent years γ-TiAl based intermetallic alloys [1–12] have been extensively studied as potential replacements for nickel-based superalloys [13–16] for different application fields, such as turbine blades for aircraft engines, stationary turbines and space vehicles. These alloys offer the opportunity for substantial weight savings when compared with Ni-based superalloys assigned for similar structural applications [17–23]. γ-TiAl based alloys show high yield strength at elevated temperatures, excellent creep characteristics and good oxidation/corrosion resistance. This combination of properties together with low density makes these alloys very attractive as high-temperature structural materials for aerospace, automotive and other industrial fields [5, 24–29].

A number of methods have been utilized in the synthesis and processing of γ-TiAl intermetallic compounds, such as Vacuum Arc Remelting (VAR), conventional melting, casting processes and powder metallurgy techniques. Conventionally, the first step is to synthesize the alloy, which is usually done by VAR or other similar technique. The shaping and processing of the material is carried out by casting techniques, typically centrifugal or gravity casting. Over the last years, a search for new synthesis approaches for intermetallic alloys (including titanium aluminide and related materials) has led, amongst others, to the technique of Self-propagating High-temperature Synthesis

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(SHS). The SHS is based on the principle of maximum utilization of the chemical energy of reacting substances (exothermicity) for obtaining inorganic compounds such as intermetallics. The SHS method was discovered in the 1970s and different technologies were developed on the basis of this method, e.g. coating synthesis, powder synthesis, welding using SHS, and one step synthesis and densification [30–41]. SHS is an environmentally friendly and energy efficient method for many materials and parts.

The objective of this work is to study one step synthesis and densification processing of γ-TiAl alloy with nominal chemical composition Ti-48Al-2Cr-2Nb (at.%) using SHS. Two different combustion routes are evaluated and optimized. Sample density, oxygen content, phase composition and microstructure are reported and discussed.

2. Materials and methods

2.1. Raw materials

The raw material selection was done according to the needs of the manufacturing technique and final product requirements. Powders with small particle size (< 100 μm) and low oxygen content were selected to prepare an alloy with composition Ti-48Al-2Cr-2Nb (at.%). Particle size, purity and chemical composition of these powders are presented in Tables 1 and 2.

2.2. Technology description

Two different combustion routes were used to produce the γ-TiAl product (see Fig. 1):

– Forced SHS + Compaction (FSHS + C)

– Thermal Explosion + Compaction (TE + C)

The FSHS + C is the typical SHS process in which the sample is locally heated until ignition occurs and a combustion wave travels through it in a self-sustaining mode converting the reagents into the product. The mechanical load is applied once the sample has reacted completely. The TE + C process is also called "Thermal Explosion", where the sample is heated until the autoignition temperature is reached. At that point the reaction starts simultaneously in the whole volume of the sample. There is no propagation front. A mechanical load is applied immediately after the reaction occurs.

Table 1. Particle size and purity of the raw materials

Material	Particle size	Purity
Titanium	−200 mesh, < 75 μm	99.5 %
Chromium	−325 mesh, < 45 μm	99 %
Niobium	−325 mesh, < 45 μm	99.8 %
Aluminium	< 200 μm	99.5 %

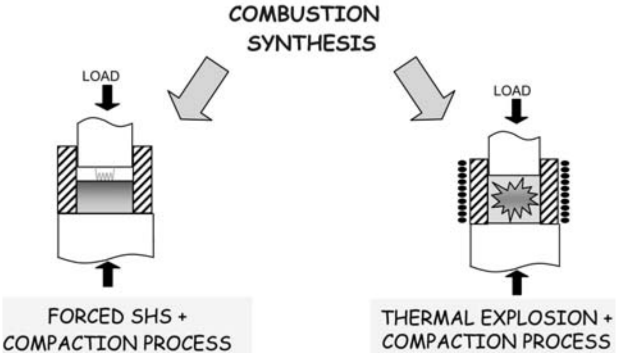

Fig. 1. Scheme of FSHS + C and TE + C reaction processes.

2.3. Experimental procedure

Both methods (FSHS + C and TE + C) started with mixing of the reagents. The powders were weighed in a balance and then dry mixed in a ball mill. After mixing the green body was prepared by cold pressing of the powders in an appropriate mould. The FSHS + C process used stainless steel dies and the samples were pressed to density of about 80 % of the theoretical density of the alloy. The TE + C route used graphite dies and the samples were cold pressed to density of about 60 % of the theoretical density. Once the green body was obtained, the FSHS + C process needed a preheating step of the sample to 350 ℃ in a furnace. The TE + C process did not require preheating.

Once heated, the FSHS + C sample was transferred from the furnace into a special mould filled with

Table 2. Chemical composition of the raw materials (wt.%)

Powder	Ti	Al	Cr	Nb	O	H	C	N
Titanium	99.7	–	–	–	0.229	0.02	0.018	0.016
Aluminium	–	99.5	–	–	–	–	–	–
Niobium	–	–	–	99.8	0.01	0.0006	0.004	0.003
Chromium	–	0.002	99.89	–	0.067	–	0.005	0.035

Table 3. Average densities of the samples

Sample	Density (g cm^{-3})	% of the theoretical value
Forced SHS + Compaction	3.98	99
Thermal explosion + Compaction (without HIP)	3.90–3.92	96.5–97.5
Thermal explosion + Compaction (with HIP)	4.00	99.5

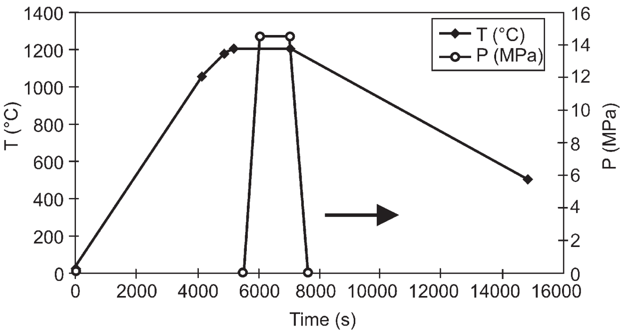

Fig. 2. Temperature and pressure cycles for thermal explosion + compaction method.

a quasi-liquid medium in order to procure an isostatic pressure. The mould was placed into the hydraulic press and the combustion reaction was initiated with an electric coil. The reaction time was derived from the combustion velocity that was established in the course of the process optimization (1.5 mm s^{-1}). A thermocouple placed in the reactor during the synthesis ensured control of the combustion reaction. The billet compaction started immediately after completion of the combustion.

Regarding the TE + C process, the graphite mould was placed into the hot press. Then the thermal and load cycle was programmed and the reaction took place. The main reaction parameters such as temperature and pressure cycles were optimized. Figure 2 shows the typical temperature and pressure cycles.

Finally, a homogenization thermal treatment was performed for both processes to obtain desired microstructure and complete chemical and microstructure homogenization. This treatment was carried out above the α (Ti-based solid solution with hexagonal crystal structure) transus temperature of this material (1364 ℃) [42] using the following parameters: inert Ar atmosphere, heating and cooling rate of 250 ℃/h, maximum temperature of 1375 ℃ and a hold time at the maximum temperature of 1 h. In addition to TE + C process, the samples required further densification. Therefore, Hot Isostatic Pressing (HIP) was carried out in order to reduce the porosity below 1 %. The main parameters of this cycle were: maximum temperature of 1260 ℃, holding time of 4 h and maximum pressure of 200 MPa.

2.3.1. Material characterization

Density was measured by the Archimedes method. A Mettler AE 240 type weight balance was used for weighting the samples. Phase analysis was performed by X-ray diffraction (XRD) using Siemens D500 apparatus working with a copper anode with a wavelength of 0.154 nm (monochromatic radiation). This diffractometer can scan 2-theta angles from 10 degrees to 90 degrees at 40 kV and 30 mA. Step increment was 0.1 degrees and counts were collected for 4 s at each step. The oxygen content in the processed material was determined by chemical analysis. The oxygen was measured as carbon dioxide and carbon monoxide using a LECO automatic analyser. Microstructure and semi-quantitative chemical composition were analysed using light microscopy and Jeol JSM 5910 LV Scanning Electron Microscope (SEM) with associated Oxford Inca 300 energy dispersive spectroscopy probe (EDS).

3. Results and discussion

3.1. Density

Table 3 shows the obtained density values. It should be emphasized that the FSHS + C route gives very high density values. On the other hand, the TE + C method needs an additional densification step (HIP) to reach the same degree of densification. The final density obtained after the HIP process is slightly higher than that obtained with the FSHS + C method. Both processing routes give porosity lower than 1 %. It is worth noting that the obtained density values are in agreement with the typically specified density for this type of material and applications (generally density of about 99 % of the theoretical values is required).

3.2. Crystallographic phases

Using both experimental routes, two phases were obtained after the SHS synthesis: γ-TiAl (face-centered tetragonal Ll_0 structure) as the main phase and α_2-Ti_3Al (hexagonal DO_{19} structure) as the minor phase. Figures 3 and 4 show the evolution of the phases before and after the thermal treatment using both FSHS + C and TE + C processes, respectively.

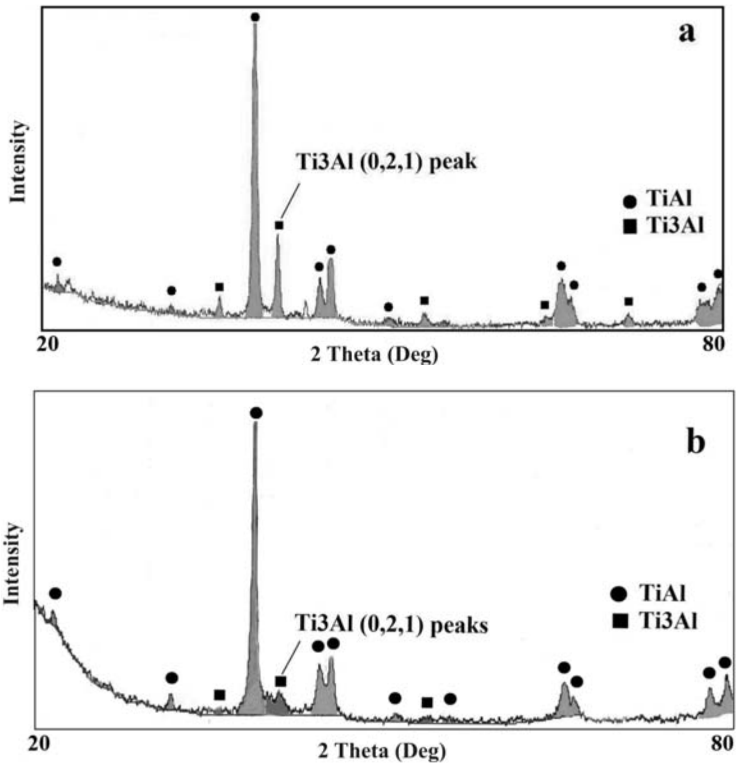

Fig. 3. FSHS + C XRD patterns: (a) after the synthesis process and (b) after thermal treatment.

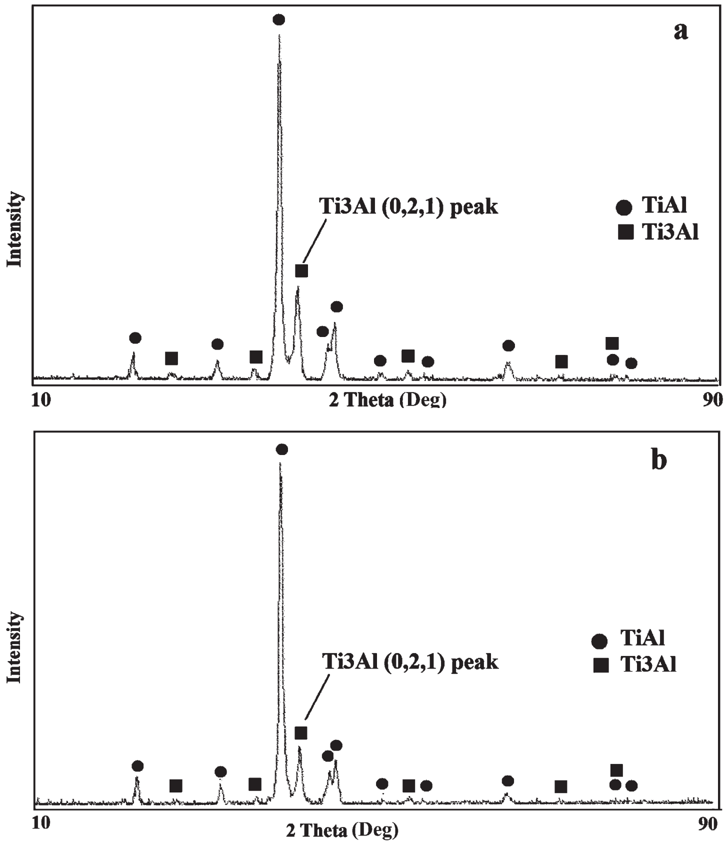

Fig. 4. XRD pattern of TE + C process: (a) after the synthesis process and (b) after thermal treatment.

Table 4. Oxygen content

Sample	Oxygen content (wt.%)
Average content in the starting reagents	0.50
Forced SHS + Compaction	0.07
Thermal explosion + Compaction	0.52

As confirmed by the intensity decrease of the (021) peaks, after the thermal treatment the amount of the α_2-phase decreases.

It can also be observed that the XRD patterns show no evidence of pure metallic Ti, Al, Nb or Cr phases in the as-reacted samples. However, since the XRD was performed on the surface of as-synthesized samples where the reaction is very intensive and assuming that the detection limit of the apparatus is about 5 to 10 vol.% of the individual phases, such results cannot be considered as evidence of a complete conversion of the reactants into the two phase intermetallic product.

3.3. Oxygen content

Oxygen content affects properties of the TiAl-based alloys and its increase has a detrimental effect on the room temperature ductility [43, 44]. Therefore, it is important to minimize the oxygen content in the final products.

Table 4 shows the oxygen content in three different samples. Firstly, the amount of oxygen in the reagents mixture was measured. It can be seen that the mixture has 0.5 wt.% of oxygen. It is then remarkable that the processing routes did not increase significantly the oxygen content. The FSHS + C route actually decreases the oxygen content. This is probably due to the self-purification nature during the self-propagating high-temperature synthesis combined with the densification process and followed by the vacuum thermal treatment. The vacuum thermal treatment had two main steps: (i) first step at 900 ℃ and (ii) second step at 1250 ℃ in a vacuum of 10^{-3} Pa. High temperature of the combustion wave may expel volatile impurities leading to higher purity products. The set of the final samples without vacuum thermal treatment has the oxygen content of about 0.2–0.5 wt.%. On the other hand, the TE + C process does not reduce the oxygen amount, but neither increases it. Figure 5 shows graphically the oxygen content of the products obtained by both synthesis routes.

3.4. Microstructure

According to the final product specifications, a fully lamellar microstructure is required. The as-synthesized sample microstructures do not present such a lamellar structure, as shown in Figs. 6 and 7. Figure 6 shows the microstructure obtained just after the synthesis of both the FSHS + C (Fig. 6a) and TE + C (Fig. 6b) samples.

It can be observed in Fig. 6 that the microstructure obtained in both cases just after the synthesis is very similar. However, this microstructure is inhomo-

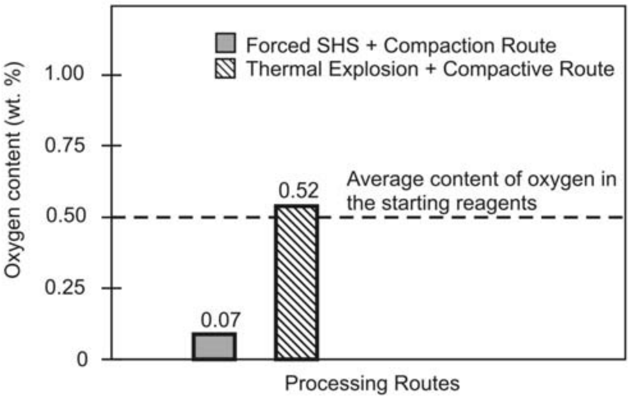

Fig. 5. Oxygen content in the products.

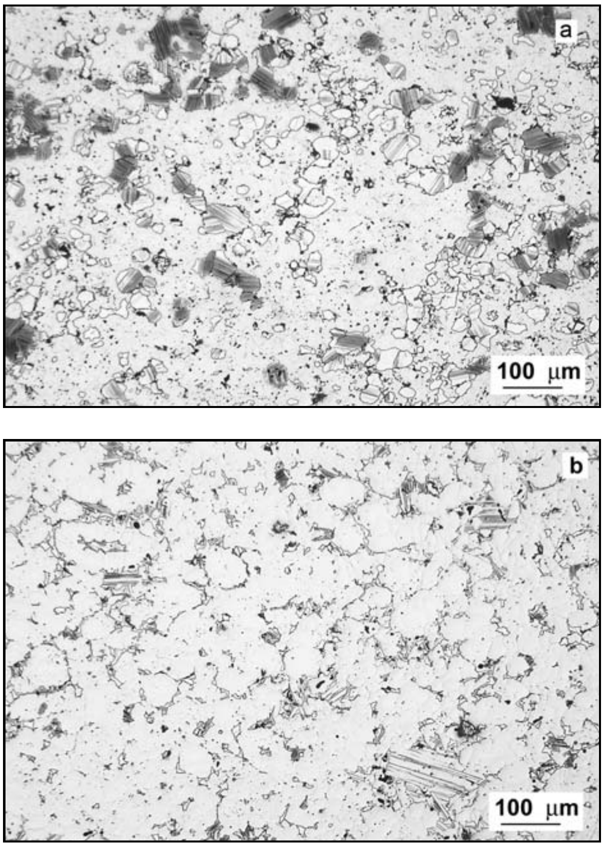

Fig. 6. Light microscopy micrographs showing: (a) FSHS + C and (b) TE + C samples after the synthesis.

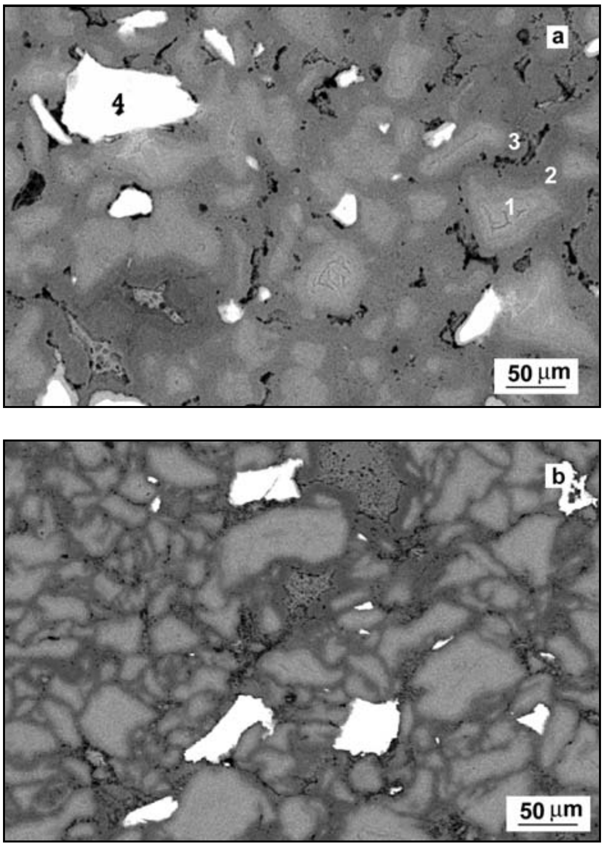

Fig. 7. SEM micrographs showing: (a) FSHS + C and (b) TE + C samples after the synthesis.

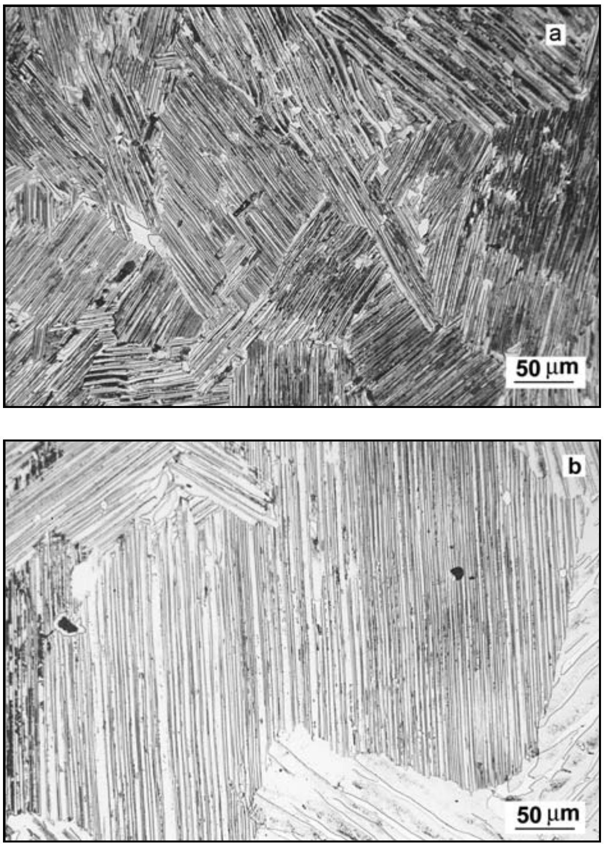

Fig. 8. Light microscope micrographs showing (a) FSHS + C and (b) TE + C samples after the thermal treatment.

Table 5. Chemical analysis (wt.%)

Zone	Al	Ti	Cr	Nb
1	–	99	–	–
2	15	85	–	–
3	70	28	2	–
4	1	3	–	96

geneous and some unreacted particles can be observed. As SHS is a fast process having duration from seconds up to few minutes, diffusion is limited and particles of intermediate products remain in the samples.

Looking more closely at the as-synthesized samples by SEM, it can be seen that the microstructures obtained by FSHS + C and by TE + C processes are very similar, as shown in Fig. 7. In addition, the chemical analysis shows an identical distribution of elements along the samples for both processing routes. Four different zones can be identified:

1. The core of the titanium particles, where no aluminium diffused into titanium particles during the synthesis.
2. The surface of the titanium particles where some aluminium is present and the main element is titanium. EDAX analysis gives a ratio close to 3 : 1 between titanium and aluminium which suggests the presence of Ti_3Al phase.
3. The matrix which surrounds the particles contains mainly aluminium with some titanium and chromium. The EDAX analysis suggests that $TiAl_3$ could be present in this zone.
4. Niobium rich particles. It appears that this element needs a longer holding time at high temperatures to be fully dissolved in the alloy.

These microstructural observations indicate that the synthesis mechanism starts with the melting of the aluminium which then reacts with titanium to form other compounds. According to the phase diagram, if the process is completed, the resultant compounds should be TiAl and Ti_3Al [29]. The analysis carried out by SEM confirms that the as-synthesized samples show a non-uniform microstructure where the diffusion of the reactants has not been completed, resulting in formation of intermediate reaction compounds. It was therefore essential to perform a thermal treatment, not only to obtain the desired lamellar microstructure, but also to homogenize the microstructure. The thermal treatment was carried out above

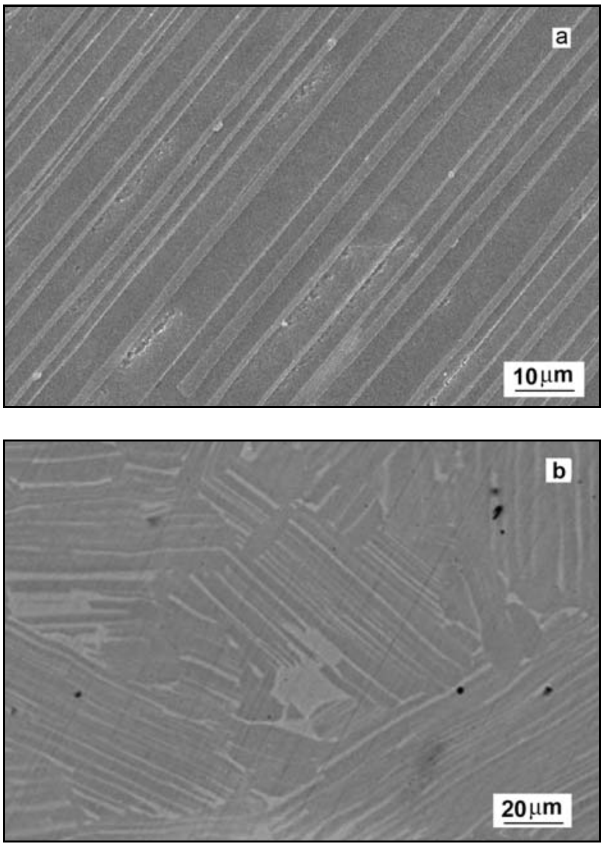

Fig. 9. Lamellae distribution in TE + C samples within: (a) single grain and (b) grains with different orientations.

the α transus temperature of this material. After the thermal treatment the microstructure is almost fully lamellar and contains only TiAl and Ti_3Al phases. Figure 8 shows an example of the obtained microstructures for both manufacturing routes. It is clear that the heat treatments result in regular α_2/γ lamellar structure for both types of samples. However, the TE + C samples show a coarser microstructure which is probably caused by the additional HIP process. The FSHS + C samples show a grain size of about 50–60 µm while TE + C samples show a grain size of about 350 µm.

SEM analysis shows uniform α_2/γ lamellae within a single grain (Fig. 9a) and different lamellar orientation from one grain to the other (Fig. 9b).

Niobium and chromium distribution was also studied by SEM using BSE mode. Figure 10a shows the distribution of niobium and chromium. The light zones are rich in niobium as confirmed by the analysis and are relatively homogeneously distributed in the volume (Fig. 10b). There are no zones with a great amount of Cr, which is homogenously dispersed in the matrix, as confirmed by the analysis shown in Fig. 10c.

Table 6 shows the required properties and their comparison with the values obtained by both FSHS + C and TE + C processing routes. It is clear that FSHS + C samples fulfilled all requirements and this process can be considered to be perspective for processing of titanium aluminides. However, the mechanical properties of such material have to be studied and compared to those measured in samples prepared by other melting and casting methods to make a final decision about the real potential of this relatively cheap and energy saving technology for industrial production of TiAl-based alloys and components.

4. Conclusions

The investigation of one step synthesis and densification processing of γ-TiAl based alloy with chemical composition Ti-48Al-2Cr-2Nb (at.%) using SHS suggests the following conclusions:

– The porosity of the samples prepared by FSHS + C and TE + C processing routes can be below 1 %.

– The samples prepared by both FSHS + C and TE + C processing routes show high chemical heterogeneity with undissolved titanium and niobium particles and non-uniform microstructure. Additional thermal heat treatment is necessary to prepare the samples with required uniform microstructure.

– The oxygen content in the final products is not higher than that of the initial reagents mixture. Hence, during the processing the oxygen content can be controlled by an appropriate raw material selection. Using low oxygen starting powders results in low oxygen content in the final products.

– The FSHS + C route produces a marked oxygen decrease in the final products compared with the initial powder mixture.

Table 6. Comparison of the obtained results with the requirements

Parameter	Requirement	FSHS + C	TE + C
Density (% of the theoretical value)	99	Fulfilled	Fulfilled
Pores	No pores > 0.1 mm	Fulfilled	Fulfilled
Oxygen content (wt.ppm)	2500	Fulfilled	Not fulfilled
Crystallographic phases	γ-TiAl and α_2-Ti_3Al	Fulfilled	Fulfilled
Microstructure	Fully lamellar	Fulfilled	Fulfilled

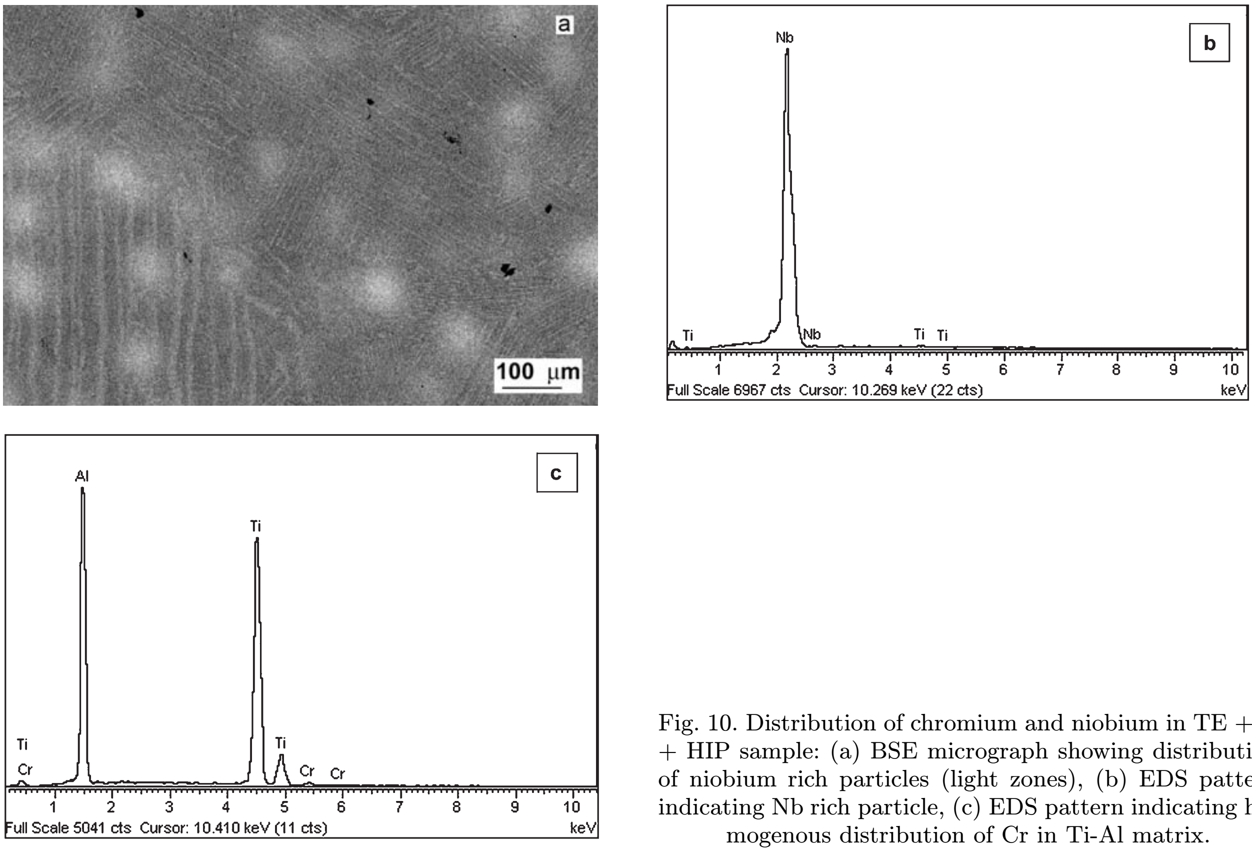

Fig. 10. Distribution of chromium and niobium in TE + C + HIP sample: (a) BSE micrograph showing distribution of niobium rich particles (light zones), (b) EDS pattern indicating Nb rich particle, (c) EDS pattern indicating homogenous distribution of Cr in Ti-Al matrix.

– After applied thermal treatment the microstructure of the samples is fully lamellar consisting of γ-TiAl (main phase) and α_2-Ti_3Al phases. All alloying elements are uniformly distributed in the samples.

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