DIRECT SYNTHESIS OF TITANIUM ALUMINIDES BY SPECIFIC METHODS OF POWDER METALLURGY

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In a first stage of research titanium aluminides have been synthesized, by means of pulsed electric current assisted sintering (SPS), followed by/ without vacuum thermal processing. Subsequently, the synthesis of titanium aluminides was attempted by maintaining metal powder compacts Al-Ti powder mixtures in gaseous environments obtained by burning urban fuel gas at temperatures below and above the melting temperature of Al, respectively.The experimental researches demonstrated a close connection between the type of the aluminides obtained, the proportion of the Al in the initial elemental powder mixture and the processing temperature. The electric current assisted synthesis of Ti-aluminides performed in vacuum, below the Ala melting temperature, led to the preponderant development of $TiAl_3$ *in the powder mixture. Further vacuum thermal processing increases significantly the Ti and Al elemental powder mixtures conversion rate in Ti-Al intermetallic compounds (e.g. about 98% for the rich Al powder). The synthesis of urban fuel gas has highlighted the possibility of occurrence and other hardening phases together with Ti-aluminides, titanium oxides and carbide phases, and* Al_2O_3*, respectively.*

Keywords: titanium aluminides, reactive synthesis, spark plasma sintering (SPSP), vacuum synthesis, urban fuel gas synthesis

1. Introduction

The intermetallic compounds (IMCs) of Al-Ti system represent a class of advanced materials with remarkable characteristics both as theoretically and practically: high melting temperatures (above 1300 ^oC), low densities (below

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4x10[3] kg/m[3]), high rigidity, strong oxidation resistance at high temperatures, resistance to the action of the environment, mechanical resistance, reliability in exploitation and others. These aspects recommend them for various applications: components of aircraft engines and space vehicles, monolithic concepts or as reinforcing phases in composites structures. These materials combine both the characteristics of metals and ceramics and presents different atomic arrangement (atomic order at high distance) by comparison with the conventional metallic alloys [1]. The beneficial properties result from their particular atomic structure (two or more sub-networks define their atomic structure). The Ti-aluminides can occur on several routes, one of them being the powder metallurgy techniques - mechanical alloying, reactive sintering, and pulsed electric current assisted sintering (SPS). The heating mode can be: i) self-propagating high-temperature synthesis (initiated by point-heating of a small part of a powder mixture/compressed part up to the exothermic reaction temperature followed by self-propagation of the exothermic reaction in all volume); ii) the thermal explosion (in-bulk heating of powder mixture/ compressed part at a constant heating rate up to the thermal explosion reaction is initiated and developed). Bertolino et. al. studied the reactive synthesis in the Ti-Al system, noticed that the temperature at which the combustion is initiated is 1191±10 ^{0}C [2] The researches on the Ti-Al system alloys (Fig. 1) concluded that these are crystallizing in the *fcc* system (including the IMCs of Ti_3Al, Ti_2Al, TiAl, $TiAl_2$ and $TiAl_3$), *hcp* and *bcc* [3].

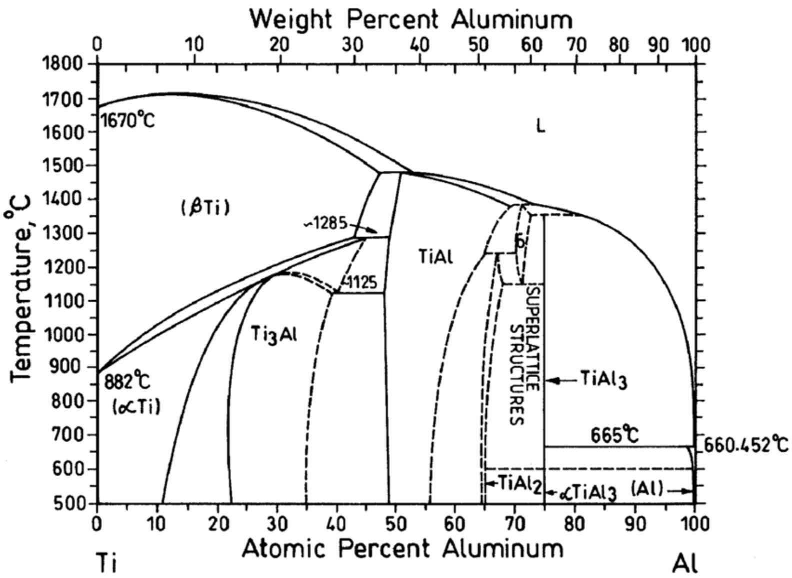


Fig. 1. Ti-Al binary phase diagram [3].

Thermodynamically, the $TiAl_3$ is the most stable phase which can develop in the Ti-Al (Fig. 2), following to the Ti and Al interaction [4].

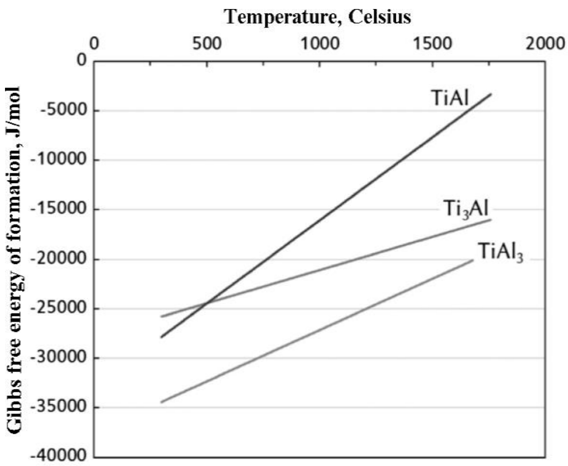


Fig. 2. Gibbs free energy of formation calculated for Ti-aluminides [3].

$TiAl_3$ and in a certain proportion, also the $TiAl_2$, has the main characteristics of the Ti_xAl type Ti-aluminides (high melting temperature, low density, significant resistance against oxidation, etc.), but also a high fragility, which recommend them as reinforcing phases in the composite materials [5]. The characteristics of $TiAl_2$ are between those related to the TiAl and $TiAl_3$.

2. Materials and Methods

Experimental researches have been realized in order to synthesize the titanium aluminides by means of Spark Plasma Sintering (SPS) followed by/without vacuum thermal processing; the aim was also to highlight the effects of sintering the compacts made from mixtures of Ti and Al elemental powders (mixing was carried out in balls mills with a useful volume of 2.5 l for 2 h, at a ratio of the milling mass bodies and the respective mass of the powder mixture of 11:1) in gaseous products made by combustion of urban fuel gas, on the conversion rate into Ti-aluminides and on the possible side effects determined by the presence of the fuel and oxidizing elements in the composition of the gaseous environment. Ti and Al powders with purities above 99 %, obtained by atomization with particles mean sizes higher than 40 μm (max.100 μm) have been utilised. The two pure metals powders have been mixed in different atomic ratios (Al:Ti=1:3÷3:1) in ball mill, with workload of 2.5 l, for 2h, at a ratio of masses of milling bodies and powdered mixtures of 11:1.

The SPS was made in a HPD5 installation (producer FCT Germany) in vacuum (10^{-6} mbar). Further thermal processing was realized also in vacuum (10^{-6} mbar). For the synthesis variant in gaseous reaction products, result by burning urban fuels from the industrial network (the composition of the urban fuel from the industrial network: about 84 %CH_4+10 %H_2+3 %N_2+2 %CO+balance %(O_2+CO_2)), mixtures of Al and Ti powders, in atomic proportions varying within the limits 1:3÷3:1, with average particle diameters over 40 μm (max.100 μm), were subject to compression at a hydraulic press, at 730 MPa and then sintered according to the thermal regime 650 ^{o}C/0.5 h → 900 ^{o}C/1.5 h, in a gaseous environment resulting from the combustion of urban fuel gas.

The experimental results have been analyzed by X-Ray diffraction (Bruker-AXS D8ADVANCE and Rigaku SmartLab Diffractometer). Scanning electronic microscopy, including Energy-Dispersive X-ray Spectroscopy analysis (SEM/EDS), using Quanta SEM Inspect F50, were also performed to estimate the results of the synthesis processes.

3. Results and discussions

By thermodynamic point of view it is obvious that $TiAl_3$ has the highest probability of nucleation and growth [4] and also is the most stable phase which develops in the Ti-Al system following to the interaction of the Ti and Al. The verification of the experimental results, performed by means of X-ray diffraction (XRD), outlined that all Ti-aluminides appeared, aspect predictable also by thermodynamic analysis. Theoretically, according to the related literature, the synthesis of the TiAl compound is less probable to occur by direct reaction between the elemental powders, the maximum effect being evident through the interaction of the particles of the pre-alloyed powders [6]. Practically, the TiAl compound was found when processing was performed at higher temperatures than the Al melting temperature.

The synthesis of Ti-aluminides by SPS performed in vacuum, below the Al melting temperature (Fig. 3), leads to formation the majority $TiAl_3$. Thermodynamically, this compound will mostly develop for Ti:Al = 1:1 [4]. The ratio changes, in both senses, against maximum, causes a significant decrease of the Ti-aluminides proportions in the final product, most of the Ti and Al being free under these processing conditions.

The processing temperature for the Ti-Al powdered mixtures influences the reciprocal solubility of the two elements and also the values of their reciprocal diffusion coefficients. It was observed that the solubility of Al in Ti increases significantly, with over 1.5 times, in the temperature range 600÷900 ^{o}C where the experiments were developed (12÷17 at%), and the solubility of Ti in Al register also a spectacular advance due to the change of the aggregation state of the latest, namely from 0.1 at% at 600 ^{o}C, to 0.6 at% at 900 ^{o}C [7]. The rates at which occurs the mass transfer of Al through diffusion in Ti and in the Ti-aluminides enriched in Ti, namely the rates at which occurs the mass transfer of Ti through diffusion in Al and in the Ti-aluminides enriched in Al, are also sensitive to the temperatures variation.

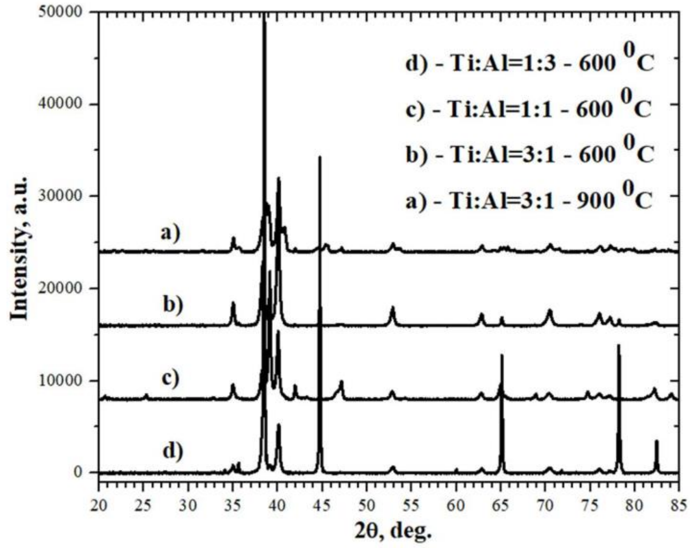
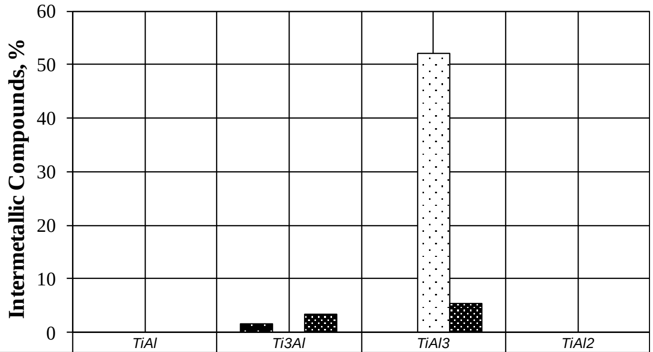


Fig. 3. XRD patterns of the reaction products in Al-Ti powdered mixtures, processed by SPS: **a)**-Ti:Al=3:1(25KN/80MPa; 650ºC/15min+ 900ºC/15min, 10^{-6}mbar); **b)**-Ti:Al=3:1; **c)**-Ti:Al=1:1; **d)**-Ti:Al=1:3 (25KN/80MPa; 550ºC/15min+600ºC/15min, 10^{-6}mbar).



	TiAl	Ti3Al	TiAl3	TiAl2
Ti:Al=1:3	0	1.43	0	0.26
Ti:Al=1:1	0	0	52	0
Ti:Al=3:1	0	3.38	5.26	0

Fig. 4 Comparative analysis of the Al-Ti IMCs types and proportion, obtained through SPS processing, in vacuum at temperatures below the Al melting temperature. (80 MPa; 550 ºC/15 min+600 ºC/15 min, 10^{-6}mbar).

The atomic percentage ration changes of the two elements (Al, Ti) in the powdered solid mixtures induces a change of the medium activity. The effect of these modifications is necessary to be correlated also with the temperature at which the synthesis takes place. Thus, at temperatures below the Al melting temperature, there are differences between the diffusion coefficients corresponding to the two elements of about 4 orders of magnitude ($D_{Al\rightarrow Ti}=1.16x10^{-13}$ m^2/s, compared to $D_{Ti\rightarrow Al}=3.05x10^{-17}$ m^2/s [8,9]. In the presented case, the maximum activity of the medium was recorded for equiatomic values of the Ti:Al ratio and was resulted in the obtaining of a higher $TiAl_3$ proportion (Figs. 3, 4).

For the synthesis processes developed with high heating rates (about 100÷150 °C/min), similar to the SPS, it is expected to develop $TiAl_3$, which is the most thermodynamically stable compound. The experimental researches confirmed these assumptions and about 52 % of $TiAl_3$ was obtained for an initial equiatomic powdered mixture. If the Al is in excess, much of it will remain unreacted in the final product, only a small part being found in the α-Ti solid solution, respectively in the intermetallic compounds: 1.43 % in Ti_3Al and 0.26 % in $TiAl_2$ (Fig. 4).

According to the principle of the transformations succession, the initiation of the Ti-aluminides synthesis process becomes possible after exceeding the maximum level of Al solubility α-Ti solid solution, at the processing temperatures of 550 °C respectively 600 °C, by concentration modification, following to the accumulation of element at the interface, from the value corresponding to the maximum solubility to the minimum value necessary to growth of the Ti-aluminides. In the case of Ti in excess, the conditions for development of about 5.26 % $TiAl_3$ and also of about 3.4 % Ti_3Al (Fig. 4), due to the diffusion of Al in the α-Ti solid solution and exceeding its solubility limit.

Another possible mechanism for the Ti_3Al and $TiAl_2$ synthesis and respectively TiAl, which could explain the decreasing of the $TiAl_3$ proportion, which is most probable to develop, is that of the direct chemical interaction between these and the Ti in excess, according to the reactions (1÷4):

$$TiAl_3 + 8Ti = 3Ti_{13}Al \tag{1}$$

$$2TiAl_3 + Ti = 3TiAl_2 \tag{2}$$

$$TiAl_3 + 2Ti = 3TiAl \tag{3}$$

$$TiAl \;\; + Ti = 2TiAl \tag{4}$$

Increasing the synthesis temperature higher than Al melting temperature (Fig. 3a), influences directly the mass transfer processes kinetics and the synthesis kinetics itself. A variety of the Ti-aluminides types and an increase of the initial Ti-Al mixture conversion rate in Ti-aluminides occur concomitantly. The coefficient of diffusion of Ti in Al at 900 °C (1.035×10^{-8} m^2/s) [10] grows by 9 orders of magnitude compared to the value registered at 600 °C (3.05×10^{-17} m^2/s) and becomes much higher than the coefficient of diffusion of Al in Ti, which shows a considerable decrease (1.17×10^{-13} m^2/s at 600 °C), compared to 7.5×10^{-14} m^2/s at 900 °C). The variations of the mass transfer rates following to the variation of the processing temperatures have to be correlated also with the variations of the reciprocal solubility of the components of the system, the highest diffusion rates being attributed to the components with the lower solubility [8].The vacuum heat processing which follows SPS (Figs. 5,6) increasing substantially the conversion rate of the Ti-Al powdered mixtures in Ti-Al intermetallic compounds (e.g. about 98 % for the rich Al powder mixtures (Ti:Al=1:3), only about 55 % for the Ti rich powder mixtures (Ti:Al=3:1)(Fig. 4).

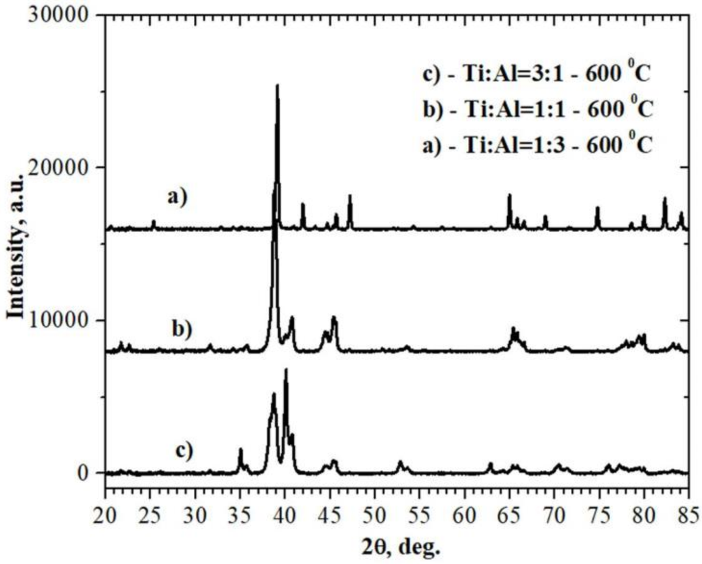
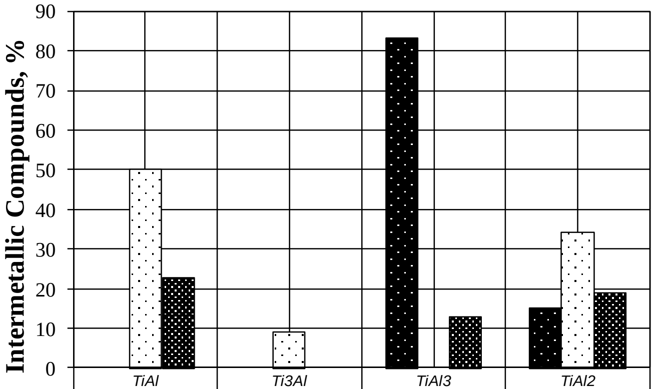


Fig. 5. XRD patterns of the reaction products in Al-Ti powdered mixtures, processed by SPS: **a)**-Ti:Al=1:3; **b)**-Ti:Al=1:1; **c)**-Ti:Al=3:1
(80MPa; 550 °C/15 min +600 **°**C/15 min, 10^{-6} mbar+550 °C/8 h+900 °C/2 h, 10^{-6} mbar)



	TiAl	Ti3Al	TiAl3	TiAl2
Ti/Al=1/3	0	0	83	15
Ti/Al=1/1	50	9	0	34
Ti/Al=3/1	23	0	12.7	19

Fig. 6. Comparative analysis of the Al-Ti IMCs types and proportions obtained through SPS processing (80MPa; 550 °C/15 min+ 600 °C/ 15 min, 10^{-6} mbar) and further thermal processing (550 °C/8 h+900 °C/2 h, 10^{-6} mbar)

Processing at temperatures above that of Al melting results in the formation of a large proportion of TiAl (about 50 %), for equiatomic mixtures of the two components and only 23 % in the case of Ti excess. The heat treatments sequence performed after the electric assisted synthesis for periods of 2÷8 hours ensures the possibility of a high conversion in the equiatomic mixtures and mainly of mixtures with excess Al.

In the case of rich Al mixtures (Ti:Al=1:3), the vacuum processing at 550 ^{o}C/8 h+900 ^{o}C/2 h, results in the formation of $TiAl_3$ (about 83 %) and $TiAl_2$ (about 15 %) which is fragile, due to the majority diffusion of Ti in Al. The presence of excess Ti diminishes the general rate of conversion, a large amount of Ti remaining as non-reactive or under the form of solid solution together with a significant amount of Al also non-reactive, but the amount is lower compared to the one measured after short term SPS processing (in the absence of the heat treatment subsequent to this processing).

The processing of Ti-Al powder mixtures in environments generated by the combustion of urban fuel gas has major implications on the phase composition of the final reaction product (Figs. 7,8).

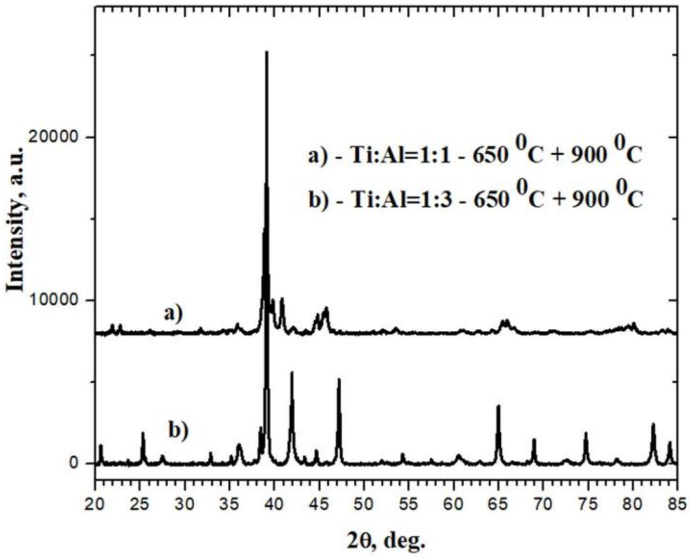


Fig.7. XRD patterns of the reaction products in Al-Ti powdered mixtures, pressed (730MPa) and subsequently sintered (650 ^{o}C / 0.5 h → 900 ^{o}C / 1.5h) in urban combustible gas.

The high chemical affinity with oxygen of Al and Ti, has as a final effect the formation of oxides (Al_2O_3, TiO_2, Ti_2O_x), and in the presence of carbon, of carbides (TiC, TiC_x), all of which contribute to diminishing the efficient transformation of the Ti-Al mixture into aluminides (Fig. 8).

It should be noted that, the maximum proportion of Al_2O_3 (86%), is found in mixtures characterized by an excess of Al (powder mixtures with ratio of atomic percents Ti:Al=1:3), decreasing to the value of about 6 % in the case of mixtures with Al deficiency (Ti:Al=3:1), so that in the case of an equiatomic composition it will increase to about 22%.

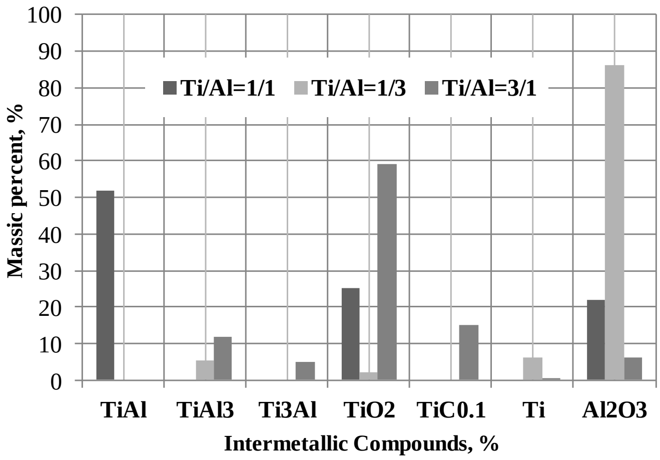


Fig.8. Comparative analyses of the IMCs and their ratio after elemental Ti-Al powder mixtures pressed (730MPa) and sintering (650oC / 0.5h → 900oC / 1.5h) in urban combustible gas.

Under the conditions of an excess of Al or Ti in the initial powder mixtures, the two elements are predominantly consumed during the synthesis of oxides or their carbides, so that there is a drastic decrease in the available Ti and Al for the synthesis of Ti-aluminides. Thus, in mixtures with Al excess (Ti:Al=1:3), the Ti and Al oxides ratio in the final product rises to about 90% (predominantly Al oxides, about 86%), and in the mixture with Ti excess (Ti:Al=3:1), the total oxides ratio and carbides amounts to 83 % (65 %, mainly Ti oxides and 18 % Ti carbides).

6. Conclusions

The results obtained from present work, in the field of Ti-aluminides synthesis by powder metallurgy techniques, can be summarized as follows:

There is a close connection between the aluminides ratio obtained and the Ti-Al atomic proportions in the initial elemental powder mixtures, and the processing temperature.

The overall kinetics of the aluminides synthesis process is dependent on the kinetics of mass transfer (diffusion processes) and the kinetics of the synthesis itself (chemical synthesis).

The highest conversion rate is reached for equiatomic ratio of the two elemental powders (Ti:Al=1:1).

The $TiAl_3$ compound is formed with the highest probability.

The synthesis of the aluminides by the SPS process, under the Al melting temperature and at short isothermal maintenance times (minutes), takes place slowly, leading to the formation of $TiAl_3$ mainly, the maximum effect being observed at the equiatomic ratio (Ti:Al=1:1); over the Al melting temperature increases the probability of obtaining Ti_3Al, as an effect of the reaction between $TiAl_3$ and the excess Ti.

The sequence of vacuum heat treatments applied after SPS, for 2÷8 h, ensures the possibility of a high conversion of the Ti-Al equiatomic powder mixtures and also of those with the excess al (Ti:Al=1:3). Over the Al melting temperature it is possible to form TiAl in a large proportion at equiatomic values of the powder mixture (Ti:Al=1:1).

Processing of Ti-Al powder mixtures in environments generated by the combustion of urban fuel gas, has major implications on the phase composition of the final reaction product:

i) the maximum conversion efficiency was recorded for the equiatomic powder composition (about 64%), in the final product of the preponderant reaction being found about 52 % TiAl;

ii) the conversion rate of the two elements into aluminides, under the conditions of processing of powder mixtures characterized by excess of Al or Ti, is extremely low (maximum 12% $TiAl_3$ in case of a mixture with Ti excess, respectively 5.3 % in the case of mixtures with Al excess).

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