Combustion synthesis of cast intermetallic Ti-Al-Nb alloys in a centrifugal machine

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Abstract

The effect of green powder composition and centrifugal overload n on combustion temperature, separation of metallic products from ceramic phases, chemical composition and microstructure of intermetallic Ti-Al-Nb alloys prepared by Self-propagating High-temperature Synthesis (SHS) in a centrifugal machine was investigated. It was found that SHS can be performed in a combustion mode by addition of energy-producing CaO_2+Al components into the product-forming $Ti + Nb + Al$ or $TiO_2 + Nb_2O_5 + Al$ powder mixtures. The yield of a metallic product increases, porosity decreases and microstructure significantly changes with increasing n. The presence of CaO in combustion products and centrifugal overload facilitates almost complete separation of ceramic phases from the metallic product. The uniform microstructure of metallic products and chemical composition close the targeted Ti-46Al-8Nb (at.%) can be achieved by an appropriate selection of SHS parameters.

K e y   w o r d s: SHS, combustion synthesis, intermetallics, cast titanium aluminides

1. Introduction

Low density, high stiffness, high creep strength and high modulus have made TiAl-based intermetallic alloys attractive material for high-temperature structural applications in the cast turbine and automotive industry [1–4]. Over past years, large research effort was devoted to a development of appropriate techniques for processing of titanium aluminides such as investment casting [1, 5], directional solidification in ceramic moulds [6] and Self-propagating High-temperature Synthesis (SHS) [7–10]. Among these techniques, the combustion synthesis (other name of SHS) means the synthesis of compounds (materials or items) in a wave of chemical reaction (combustion) that propagates over starting reactive mixture owing to layer-by-layer heat transfer. Because of a low caloricity of reaction between Ti and Al, the classical SHS reaction between these metals can be initiated only upon preliminary heating of a green mixture. For this reason, the best results in synthesis of titanium aluminides were attained by combining SHS with some kinds of internal influence, such as heating

up to the ignition temperature [8–11], mechanoactivation of green mixture [12, 13], SHS followed by hot isostatic pressing (HIP) [9, 14] and SHS in electromagnetic field [15].

The aim of the present work is to study the effect of green powder composition and centrifugal overload on the combustion temperature, formation of metal phase, chemical composition and microstructure of an intermetallic alloy with nominal chemical composition Ti-46Al-8Nb (at.%) prepared by SHS in a centrifugal machine. The method of SHS metallurgy [10, 16–22] has been selected as an alternative cheap processing route to classical investment casting [1, 5] or directional solidification of dispersion strengthened titanium aluminides in ceramic moulds [6, 23, 24].

2. Experimental

Green powder compositions were selected to obtain a cast alloy with nominal chemical composition Ti-46Al-8Nb (at.%). The product-forming components were either a mixture of pure elementary powders
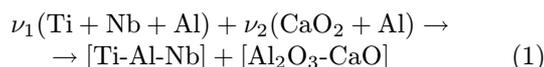

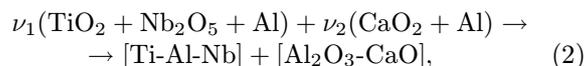*Corresponding author: tel.: 09652 46312; fax: 095 9628025; e-mail address: svn@ism.ac.ru

Reagent	Grade purity (%)	Particle size (μm)
Ti	98.60	< 80
TiO$_2$	99.56	< 40
Nb	99.92	< 100
Nb$_2$O$_5$	99.80	< 10
Al	99.80	< 40
CaO$_2$	99.70	< 10

of Ti, Al and Nb or a thermite-like mixture of significantly cheaper powders of TiO$_2$, Nb$_2$O$_5$ and Al. Since heat release during combustion of these systems is rather low, an energy-producing mixture of CaO$_2$ + Al was also added to the samples to increase the combustion temperature T_c. Corresponding reaction equations for both types of mixtures can be written in the form:

$$\nu_1(\text{Ti} + \text{Nb} + \text{Al}) + \nu_2(\text{CaO}_2 + \text{Al}) \rightarrow$$
$$\rightarrow [\text{Ti-Al-Nb}] + [\text{Al}_2\text{O}_3\text{-CaO}] \qquad (1)$$

and

$$\nu_1(\text{TiO}_2 + \text{Nb}_2\text{O}_5 + \text{Al}) + \nu_2(\text{CaO}_2 + \text{Al}) \rightarrow$$
$$\rightarrow [\text{Ti-Al-Nb}] + [\text{Al}_2\text{O}_3\text{-CaO}], \qquad (2)$$

where ν_1 and ν_2 ($\nu_1 + \nu_2 = 1.0$) are weight fractions of product-forming and energy-producing mixtures, respectively. The powders used in these experiments are characterized in Table 1.

Relative amount of Ti, Nb, and Al (or TiO$_2$, Nb$_2$O$_5$, and Al) in the product-forming mixtures as well as weight fractions of the product-forming (ν_1) and energy-producing (ν_2) mixtures were varied. The components were mixed in a planetary mill and then placed into cylindrical graphite moulds. The inner surface of the moulds was coated with a protective alumina layer. In the centrifugal machine shown in Fig. 1a, the overload $n = a/g$, where a is the centrifugal acceleration and g is the acceleration due to the gravity, attained values ranging from 50 to 1000. Sample weight used in these experiments was about 50 g. In the experiments, the weight loss $\eta = [M_0 - (M_1 + M_2)]$ during combustion was measured as a difference between the weight of the initial mixture (M_0) and the weight of the final product consisting of metallic (M_1) and oxide (M_2) phases. Preliminary experiments were performed in quartz ampoules with a diameter of $d = 16$ mm and height of $h = 70$ mm at a pressure of $P = 0.1$ MPa and $n = 1$ in air. The burning velocity was measured with the array of photodiodes 5 connected via collector 3 to a computer, as illustrated in Fig. 1b. Thermodynamic calculations were carried out by THERMO software [25].
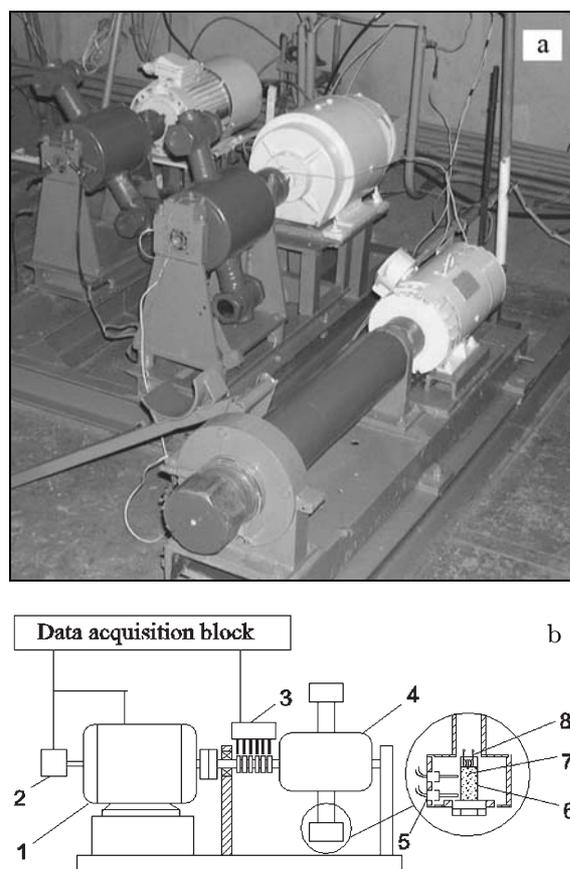

Fig. 1. Outside view (a) and sketch (b) of the centrifugal machine used in experiments: (1) electric motor, (2) tachometer, (3) collector, (4) rotor, (5) photodiodes, (6) quartz mould, (7) sample, (8) igniter.

Samples prepared by SHS were subjected to a standard chemical analysis, X-ray diffraction (XRD), scanning electron microscopy analysis, and electron-probe microanalysis.

3. Results and discussion

3.1. Calculations of combustion temperature

A prerequisite for SHS casting is that the attained combustion temperature T_c must be higher than the melting point T_m of combustion products: $T_c > T_m$ (T_m for investigated Ti-46Al-8Nb alloy is about 1888 K). As seen in Fig. 2, the results of thermodynamic calculations indicate that the values of the adiabatic combustion temperature (T_{ad}) for both types of product forming mixtures are insufficient to fulfill criteria $T_{ad} > T_m$. Due to the presence of unavoidable heat losses, real T_c values are still lower than the calculated adiabatic combustion temperature (T_{ad}). Adding the energy-producing mixture of CaO$_2$ + Al into target mixtures, T_{ad} markedly increases, which
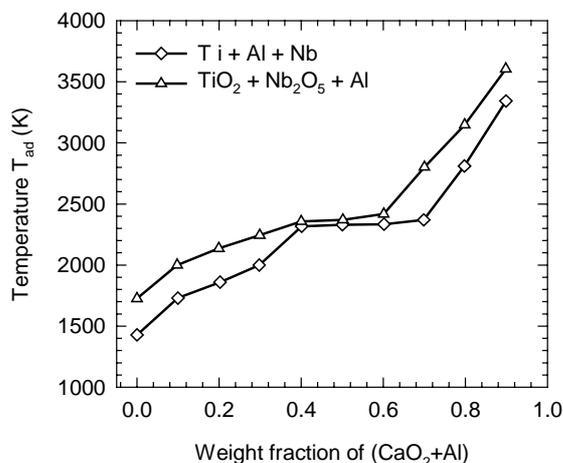
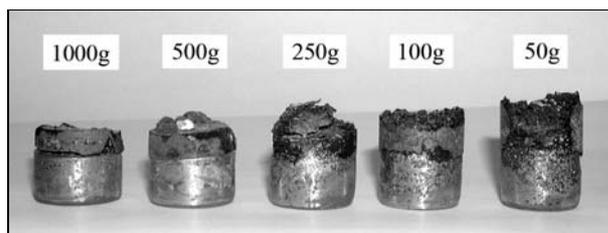Fig. 2. Dependence of calculated T_{ad} on relative weight fraction of energy-producing component (ν_2).

Fig. 3. Photographs showing ingots prepared by SHS in centrifugal machine at various centrifugal acceleration a.

Fig. 4. Outward appearance of the ingot before (a) and after (b) separation of the oxide layer from the metallic part.

allows processing of the cast intermetallic alloy in a combustion mode, as seen in Fig. 2. For $\nu_2 > 0.2$, all the products can be expected to appear in the form of a melt. In addition, the selected mixture yields the products, which are inert toward the target products (melt of Ti-Al-Nb). With increasing T_c, the amount of gaseous products (suboxides, Al vapor *etc.*) can increase, which may lead to melt splashing. In order to avoid the splashing, optimal values of ν_2 were calculated to range from 0.2 to 0.4.

3.2. Visual observations

Visually, the combustion was found to propagate at a constant rate. With increasing ν_2, the splashing of the melt becomes more and more probable. In preliminary experiments under normal conditions ($P = 0.1$ MPa, $T_0 = 293$ K, $a = 1$ g, air), optimal values of ν_2 for each product-forming mixture were determined to vary between 0.3 and 0.45. Within this range of the relative weight fractions of energy-producing components, dense titanium aluminides can be prepared in a high yield (good separation of metallic and oxide phases).

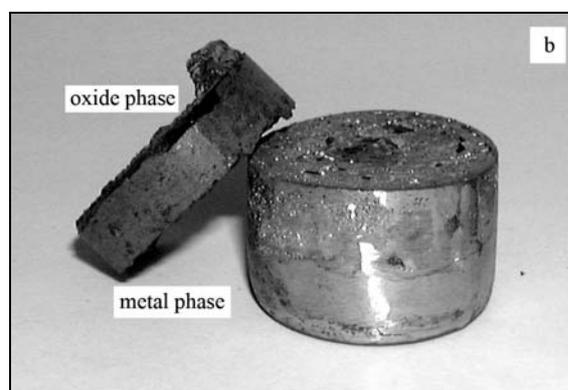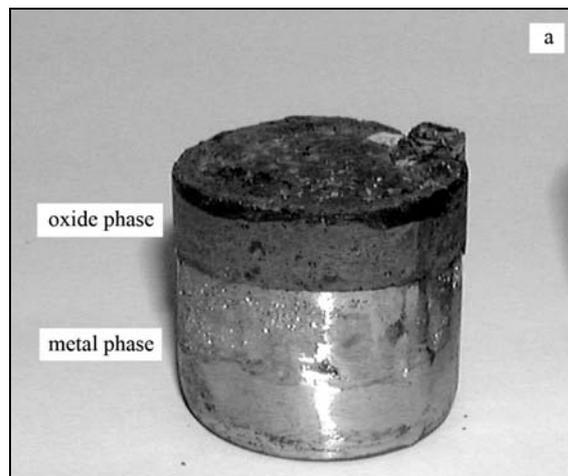The outward appearance of the samples burned at

different a is shown in Fig. 3. It is clear that the extent of phase separation increases with increasing a. The samples obtained at a ranging from 300 to 1000 g exhibit readily separated metallic and oxide layers, as shown in Fig. 4. An appropriate separation of metallic (Ti-Al-Nb) and oxide (Al_2O_3-CaO) phases is a key parameter of this process. As shown by Lapin et al. [26, 27], ceramic particles such as Al_2O_3 influence significantly mechanical properties of titanium aluminides. Increasing volume fraction of ceramic particles increases yield strength and hardness but decreases room-temperature ductility and ultimate compressive strength of TiAl-based alloys [26].

3.3. Chemical composition

Varying the relative weight fractions of components in the product-forming mixture, final chemical composition of ingots prepared by SHS in the centrifugal machine can be well controlled, which allows to achieve targeted chemical composition Ti-46Al-8Nb (at.%). The chemical and phase composition of the ingots obtained under high gravity values ($a = 700$ g)

T a b l e 2. Chemical and phase composition of cast titanium aluminides prepared by SHS

Exothermic mixture	Ingot area	Phase composition	Chemical composition (at.%)		
			Al	Nb	Ti
Elemental	top	TiAl, Ti$_3$Al	45.55	7.96	rest
	middle	TiAl, Ti$_3$Al	45.40	7.82	–
	bottom	TiAl, Ti$_3$Al	45.34	7.87	rest
Thermite-type	top	TiAl, Ti$_3$Al	45.40	7.83	rest
	middle	TiAl, Ti$_3$Al	45.24	7.91	–
	bottom	TiAl, Ti$_3$Al	45.70	7.86	rest

T a b l e 3. Chemical composition of ingots obtained at different centrifugal acceleration a

Type of green mixture	Elements	Composition (at.%)			
		50 g	250 g	500 g	1000 g
Elemental	Al	45.86	45.73	45.47	45.26
	Nb	7.82	7.82	7.91	7.87
	Ti	rest	rest	rest	rest
Thermite-type	Al	48.77	47.84	45.80	45.93
	Nb	8.21	8.43	7.91	7.96
	Ti	42.74	43.02	45.81	45.95
	others	0.28	0.71	0.78	0.16
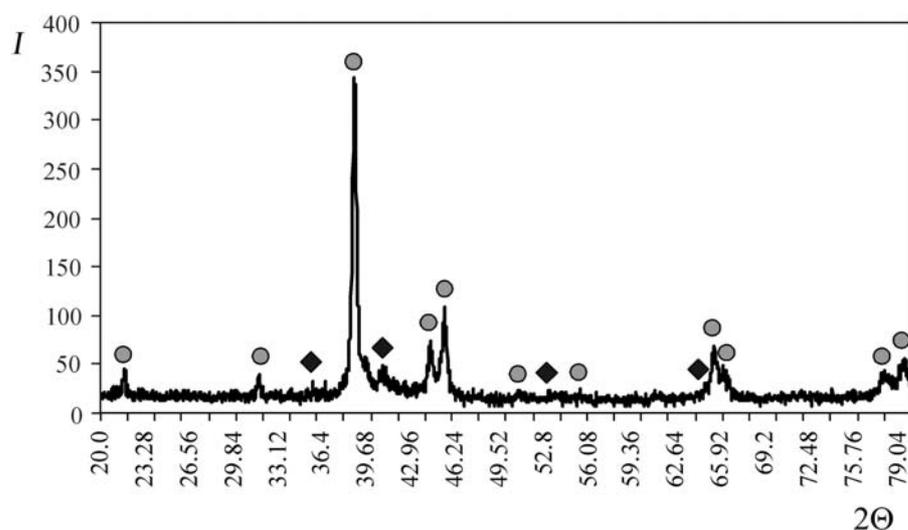
Fig. 5. The typical diffraction pattern of metallic part of ingots produced by SHS: ($\blacklozenge$) Ti$_3$Al and ($\bullet$) TiAl.

are presented in Table 2. The content of Al, Nb, and Ti varies along the sample height within 0.2 at.%, which is within the systematic error of the measurements. This is due to the gravity-assisted interfusion of components during combustion. For both systems, the phase composition (TiAl, Ti$_3$Al) was found to be virtually independent of a. It was found that Ti content slightly increases and Al content decreases with increasing a for the thermite-like mixture, as shown in Table 3. The overload a was also found to markedly hamper splashing of the melt and thus increases the yield of metallic product in agreement with our earlier data [22]. Table 3 indicates that sound titanium aluminides with targeted chemical composition and quality can be also produced by an appropriate selection of SHS parameters using significantly cheaper TiO$_2$ + Nb$_2$O$_5$ + Al type powder mixtures (thermite-type mixture).
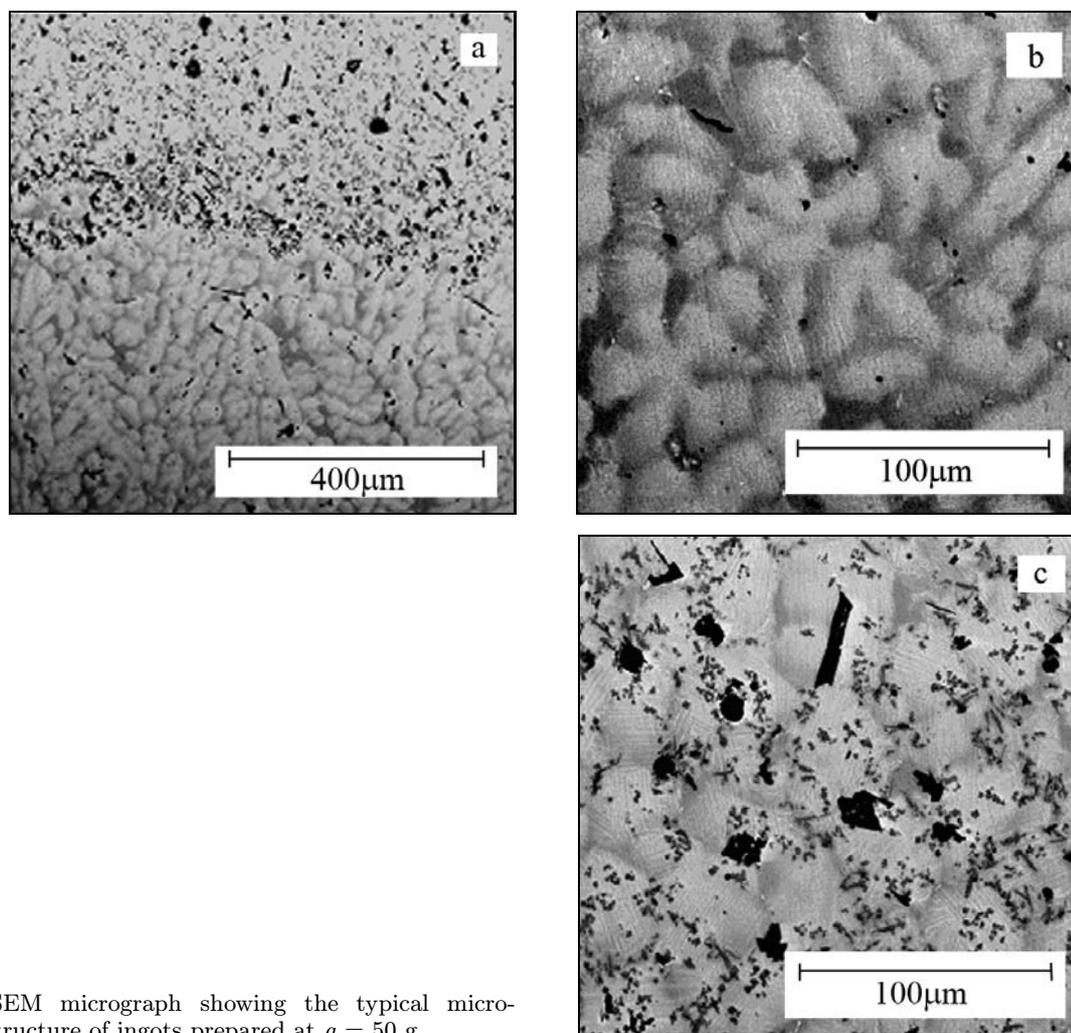
Fig. 6. SEM micrograph showing the typical microstructure of ingots prepared at $a = 50$ g.

Despite of a high Nb content in the studied alloys, no Nb-based intermetallic compounds were detected by XRD analysis. The obtained diffraction patterns exhibit only the presence of γ-TiAl and α_2-Ti$_3$Al phases, as shown in Fig. 5. According to the phase diagram, a maximum solubility of Nb in TiAl is 11 at.% while the studied alloy contains only 8 at.% of Nb. However, all diffraction peaks are shifted toward greater interplanar distances, which can be associated with formation of a solid solution of Nb in the TiAl lattice. In addition, no nitrogen-containing products were detected, which can be attributed to the protection of the melt from nitridation with atmospheric nitrogen by the slag layer formed on the melt surface. The above data confirm the prediction of the thermodynamic calculations about the inertness of the products formed upon combustion in the CaO$_2$ + Al. It should be noted that Ca-containing products are also not formed even for relative high weight fractions of energy-producing mixture ($\nu_2 > 0.5$). Preliminary measurements revealed relatively high content of oxygen ranging from about 2000 to 4000 ppm (wt.%) in the metallic part of ingots produced by SHS.

Higher oxygen level in the melt changes solidification path, promotes solidification through primary α-phase (Ti-based solution with hexagonal structure) instead of the β-phase (Ti-based solution with cubic crystal structure) and stabilizes the α-phase in the microstructure, which affects significantly microstructure and mechanical properties of the cast components [24, 26–28]. However, more oxygen measurements have to be performed on ingots prepared at various processing parameters to confirm these preliminary results.

3.4. Microstructure

Physical and mechanical properties of titanium aluminides are known to strongly depend on the microstructure [29–31], presence/absence of non-metallic inclusions [24, 26, 27] and oxygen content [32]. SEM observations showed that the ingots obtained at $a < 100$ g displayed two-layer structure without a clear layer separation, as illustrated in Figs. 3 and 6a. The bottom metallic part has a typical dendritic microstructure with residual porosity and few ceramic particles, as illustrated in Fig. 6b. The upper part
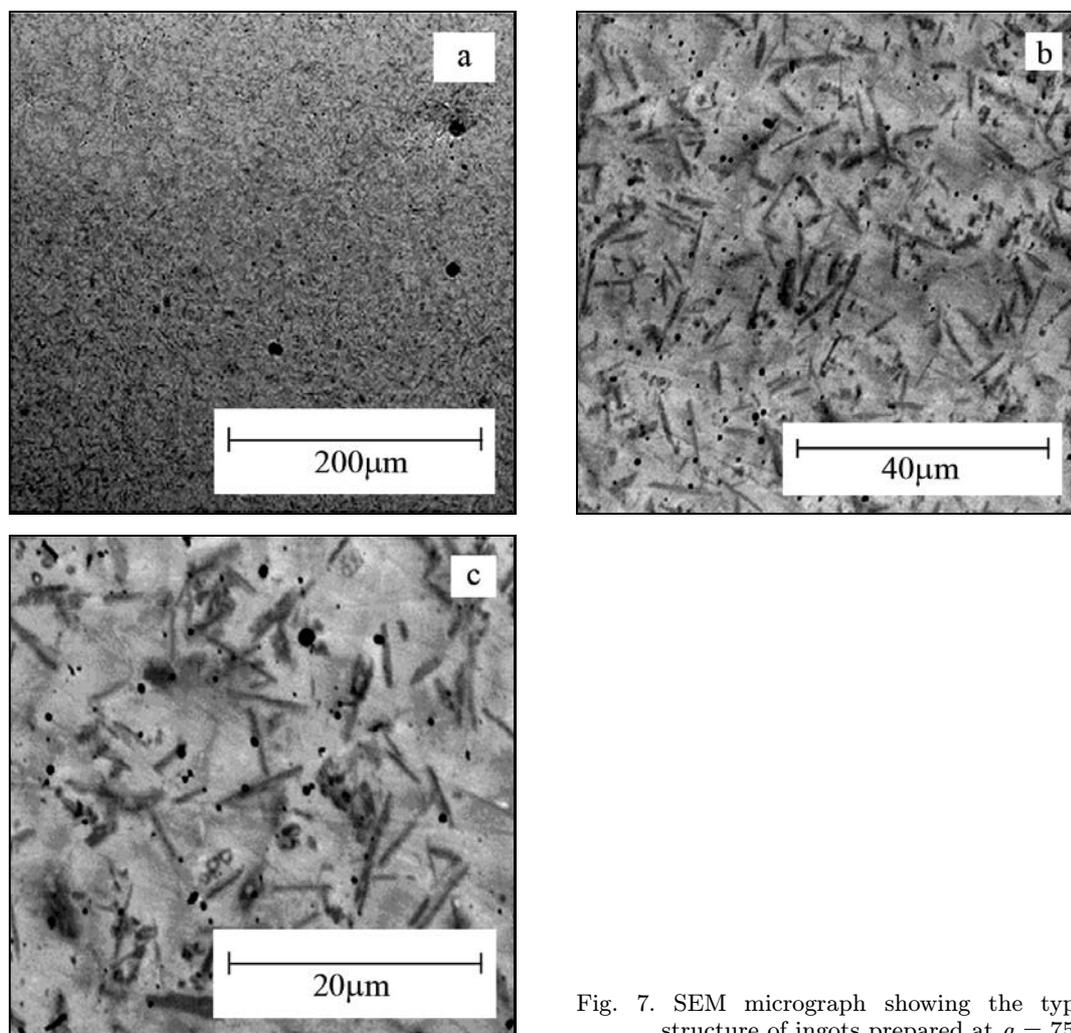
Fig. 7. SEM micrograph showing the typical micro-structure of ingots prepared at $a = 750$ g.

of ingots has numerous oxide inclusions, as seen in Fig. 6c. The ingots obtained at $a > 300$ g contained only a low amount of pores at the interface, as seen in Fig. 3. This implies that a high extent of phase separation can be only attained at a sufficiently high a. In contrast to the samples obtained at lower a, the ingots obtained at $a > 500$ g had a nice outward surface shown in Fig. 4 and corresponding homogenous microstructure shown in Figs. 7a to 7c.

4. Conclusions

The addition of the energy-producing $CaO_2 + Al$ mixture to the product-forming $Ti + Nb + Al$ or $TiO_2 + Nb_2O_5 + Al$ mixtures was found to afford processing of cast Nb-doped titanium aluminides by gravity-assisted SHS technique. The chemical composition of combustion products can be controlled by variation of initial green powder composition. The use of metal oxide powder mixtures can significantly decrease production cost of titanium aluminides. The gravity-assisted interfusion of components during combustion leads to homogenization of the chemical/phase composition over the whole volume of Ti-Al-Nb ingots. The presence of CaO in combustion products facilitates almost complete separation of ceramic phases from metallic product.

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