

## TITANIUM ALUMINIDES SYNTHESIS BY ALUMINO-CALCIOTHERMIC REDUCTION OF TiO<sub>2</sub>

A. R. Kamali<sup>1</sup>, S. M. M. Hadavi<sup>1</sup>, H. Razavizadeh<sup>2</sup> and J. Fahim<sup>1</sup>

alirezakam@yahoo.com

Date of Receive: April: 2008      Date of Acceptance: May 2008

<sup>1</sup> Department of Chemical and Materials Engineering, Malek Ashtar, University of Technology, Tehran, Iran

<sup>2</sup> Department of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran

**Abstract:** Production of titanium aluminides in TiO<sub>2</sub>-Al-Ca system has been investigated. For this purpose, different compositions of raw materials were studied in a special reaction vessel. In a special case, the non-completed reaction of TiO<sub>2</sub> with Al and Ca resulted in the production of granulates of titanium aluminides especially Ti<sub>3</sub>Al and other Ti – Al phases as the metallic product and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> as the non-metallic product. Remelting of metallic granulates led to production of TiAl ingot.

**Keywords:** Titanium Aluminide, Titanium Dioxide, Alumino-Calciothermic.

### 1. INTRODUCTION

Titanium aluminide intermetallic compounds are a new class of advanced materials with unique thermal properties such as high specific strength, excellent oxidation resistance and acceptable mechanical properties at high temperatures [1-2]. Replacement of Ni-based superalloys by  $\gamma$ -TiAl alloys in jet engine components results in considerable reduction of weight and therefore increases of speed and efficiency [3-5]. However, in order to put this material in operation for its wide applications, some challenges must be overcome. The most important challenges are their low toughness at room temperature and technical difficulties in production. The production process of titanium aluminides are divided in two categories: ingot metallurgy and powder metallurgy.

#### 1.1. Ingot Metallurgy

The ingot metallurgy includes technologies such as vacuum arc remelting (VAR) [6], vacuum induction melting (VIM) either in ceramic crucible [7] or in cold crucible [8] and electroslag remelting (ESR) [9]. These processes were used for titanium aluminides productions which all have some limits related to the control of chemical composition and expensiveness of the final product.

#### 1.2. Powder Metallurgy

The powder metallurgy processes for production

of titanium aluminides include non-reactive and reactive sintering. The non-reactive sintering is a process for production of a wide range of materials such as titanium aluminides. "Non-reactive sintering" means that the sintering is carried out only for densification with no chemical reaction. In the case of this process, the raw materials would be pre-alloyed titanium aluminides (Ti<sub>x</sub>Al<sub>y</sub>) powders. The powders are produced by atomization [10] or mechanical alloying [11-13]. Reactive sintering or self-propagating high temperature synthesis (SHS) or combustion synthesis offers an attractive alternative route for production of titanium aluminides [14]. "Reactive sintering" means that a chemical reaction is occurred during sintering process. In this process, the raw materials are elemental titanium and aluminium or compounds like TiO<sub>2</sub> powders. The SHS process has two different modes: a) plane wave propagation (PWP) mode and b) thermal explosion mode [15]. The PWP technique was adopted to produce gamma titanium aluminide (TiAl) by using of Ti and Al powders as raw materials [14]. Products of this process are a mixture of TiAl and other phases like Ti<sub>3</sub>Al, TiAl<sub>3</sub>, Ti and Al [14]. However, it seems that the thermal explosion method has not been explored much for producing titanium aluminides. It is noted that economical production is possible when Ti is replaced by a relatively low price raw material such as TiO<sub>2</sub> [16]. This attractive recent

approach is based on the following reaction [17]:  
 $3\text{TiO}_2 + 7\text{Al} = 3\text{TiAl} + 2\text{Al}_2\text{O}_3$  (1)

Product of reaction 1 is a composite comprising of titanium aluminide and alumina powders. It is reported that this composite can be a non-expensive alternative for some components in engines [18]. The goal of this research is reduction of  $\text{TiO}_2$  with Al in presence of Ca to produce non-composite titanium aluminides.

## 2. EXPERIMENTAL

### 2.1. Materials

The elemental powders, Al (merck, <math>100\mu\text{m}</math>, 99.95%),  $\text{TiO}_2$  (merck, <math>150\mu\text{m}</math>, 99.98%), and Ca (merck, granulated, 99.95%) were used as raw materials. The reactions were performed in an  $\text{Al}_2\text{O}_3$  crucible (99.95%).

### 2.2. Idea of Research

The reaction between  $\text{TiO}_2$  and Al results in the formation of a mixture consisting of alumina and titanium aluminides [17]. According to reaction 1, the product of reaction can be TiAl and  $\text{Al}_2\text{O}_3$ . The melting point of TiAl is about 1500 °C (Fig. 1) and that of  $\text{Al}_2\text{O}_3$  is 2000°C [20]. In order to have a metallic and a slag phase in separated form, it is necessary to add an additive to  $\text{TiO}_2$  and Al raw materials. In this case, it seems that CaO is a suitable option based on the  $\text{Al}_2\text{O}_3$ -CaO binary phase diagram (Fig. 2) [21]. Therefore CaO can be used as an additive to reduce the melting point of slag. In order to bring CaO into the reaction system, Ca powder can be added to raw materials.

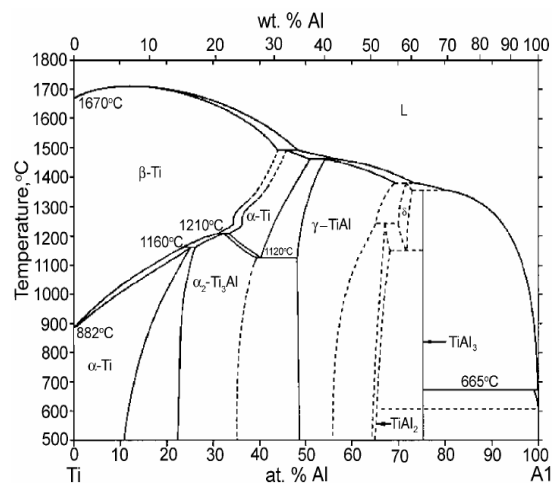


Fig. 1. Ti-Al phase diagram [8].

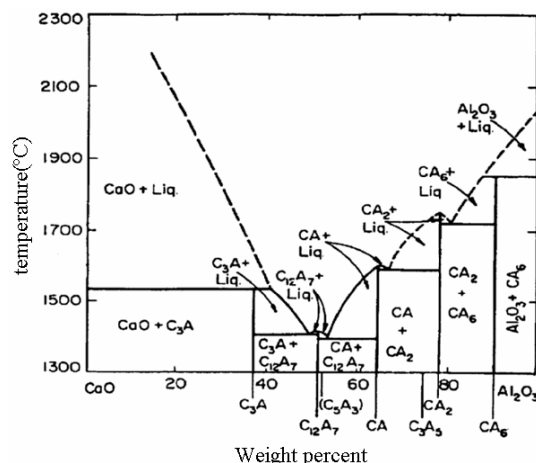


Fig. 2. CaO- $\text{Al}_2\text{O}_3$  phase diagram [12].

### 2.3. Procedures

The powders of raw materials were combined and mixed by a mixer. The mixed powders were placed in an alumina crucible and pounded by a mallet. The crucible then sealed by means of a ceramic bung. The crucible was placed in a flanged steel vessel where the empty space within the vessel was filled with MgO or  $\text{Al}_2\text{O}_3$  powder. The presence of MgO or  $\text{Al}_2\text{O}_3$  powders is desirable for preventing damage to ceramic crucible which may occur as a result of severe shocking during the reaction and also preventing oxygen diffusion to the crucible. The steel vessel was sealed by means of screwing with a steel bung (Fig. 3). The steel vessel then was placed into an electric furnace. The heating of the furnace was carried out with the rate of 20°C/min to 1000 °C. After 20 minutes when the reaction was completed, furnace was turned off. After ensuring the cooling of vessel to about room temperature, the vessel was removed. The detail of this process has been explained elsewhere [19].

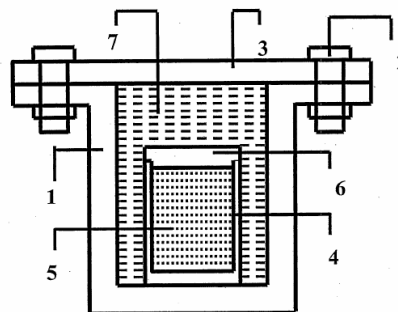


Fig. 3. The experimental setup. 1: steel vessel, 2: screw, 3: steel bung, 4: crucible, 5: mixed charge, 6: alumina crucible bung, 7: ceramic powder.

**Table 1.** Amount of raw materials according to different reactions and obtained product.

	Considered Reaction	Amount of raw material (g)			Ca/TiO <sub>2</sub> mole ratio	Product
		TiO <sub>2</sub>	Al	Ca		
1	19TiO <sub>2</sub> + 43Al + 2Ca = 2CaAl <sub>12</sub> O <sub>19</sub> + 19TiAl	10.55	8.05	0.55	0.105	powder
2	7TiO <sub>2</sub> + 15Al + 2Ca = 2CaAl <sub>4</sub> O <sub>7</sub> + 7TiAl	10.87	7.86	1.54	0.286	Powder
3	2TiO <sub>2</sub> + 4Al + Ca = CaAl <sub>2</sub> O <sub>4</sub> + 2TiAl	10.66	7.20	2.66	0.500	Powder
4	33TiO <sub>2</sub> + 61Al + 24Ca = 2Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> + 33TiAl	12.56	7.82	4.56	0.727	Metallic and non-metallic granulates
5	3TiO <sub>2</sub> + 5Al + 3Ca = Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> + 3TiAl	12.00	4.05	6.00	1	powder

### 2.4. Analyzing of Products

Characterization of products was performed by X-ray diffraction (Siemens Kristalloflex 810 equipped with a copper anode operated at 40KV and 30mA, with graphite curved monochromatic on the diffracted beam). The microscopic study was performed by using optical microscopy and scanning electron microscopy (SEM) equipped with EDX analyser. The samples were etched in a solution of modified knoll's reagent (5%HF, 15%HNO<sub>3</sub>, 80%H<sub>2</sub>O).

## 3. RESULTS AND DISSCUTION

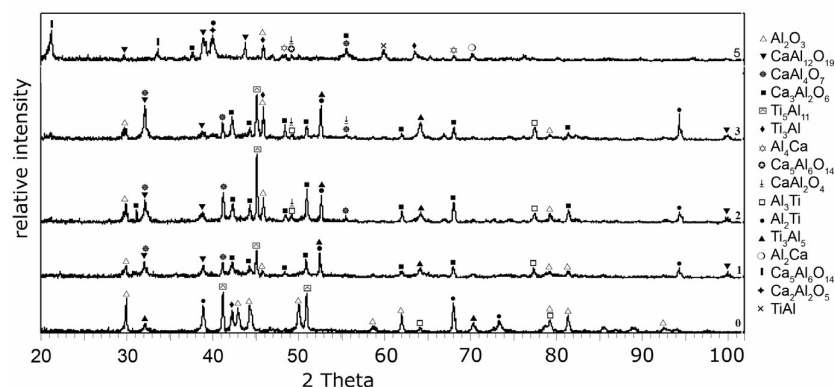
### 3.1. Alumino-Calciothermic Reduction of TiO<sub>2</sub>

TiAl and calcioaluminates can be formed during the reaction between TiO<sub>2</sub>, Al and Ca according to Table 1. It can be found from Table 1 that only in reaction 4, the product comprised the metallic and non-metallic granulates. In other cases, powder products were obtained. X-ray diffraction patterns of products of reaction 1, 2, 3 and 5 (Table 1) are presented in Fig. 4. In Fig. 4, The XRD labeled to "0" is related to "3TiO<sub>2</sub>+7Al = 3TiAl+2Al<sub>2</sub>O<sub>3</sub>". The product of

different reactions according to Fig. 4 is shown in Table 2.

It is seen from Table 2 that according to reaction 1,2,3 and 5, powders comprising of some titanium aluminides and calcioaluminates were produced with adding of Ca to TiO<sub>2</sub>+Al raw materials. With increasing of Ca, in reaction 5, an intermediate phase of Al-Ca (Al<sub>4</sub>Ca) also was formed. Therefore some of the reactant that can contribute in production of titanium aluminides was consumed. On the other hand, as it is seen in Table 2, heating of raw materials according to reaction 4 caused to formation of metallic and non-metallic granulates.

This experiment was repeated with different amount of raw materials and same results were obtained (Table 3). One of the products in reaction 4 was Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. This phase has the lowest melting point in CaO-Al<sub>2</sub>O<sub>3</sub> phase diagram. Therefore the released heat during the reaction 4 was resulted in the partially fusion of the slag and metallic product. The presence of Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> as a major peak in products is due to the partially fusion and therefore partially completion of reaction.



**Fig. 4.** X-ray diffraction patterns of products of reaction 1, 2, 3 and 5 (Table 1).

**Table 2.** The product of different reactions.

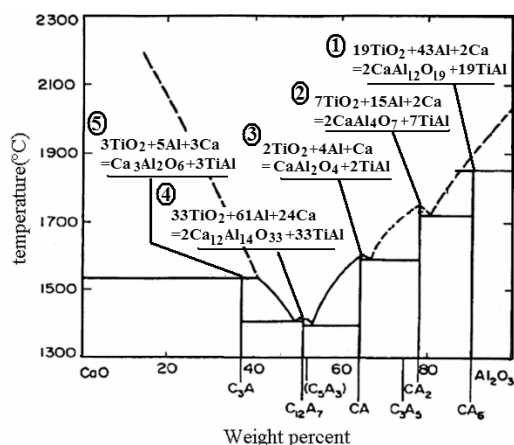
Reaction Number (table1)	Considered Reaction	Product		
		Titanium Aluminides	Calcium Aluminates	Other phases
0	$3\text{TiO}_2 + 7\text{Al} = 3\text{TiAl} + 2\text{Al}_2\text{O}_3$	$\text{TiAl}_2\text{-Ti}_3\text{Al}_5\text{-TiAl}_3$	-	$\text{Al}_2\text{O}_3$
1	$19\text{TiO}_2 + 43\text{Al} + 2\text{Ca} = 2\text{CaAl}_{12}\text{O}_{19} + 19\text{TiAl}$	$\text{Ti}_3\text{Al}_5\text{-TiAl}_2$	$\text{CaAl}_{12}\text{O}_{19}\text{-Ca}_3\text{Al}_2\text{O}_6$	$\text{Al}_2\text{O}_3$
2	$7\text{TiO}_2 + 15\text{Al} + 2\text{Ca} = 2\text{CaAl}_4\text{O}_7 + 7\text{TiAl}$	$\text{Ti}_3\text{Al}_5\text{-TiAl}_2\text{-TiAl}_3$	$\text{Ca}_3\text{Al}_2\text{O}_6\text{-CaAl}_4\text{O}_7\text{-CaAl}_{12}\text{O}_{19}$	$\text{Al}_2\text{O}_3$
3	$33\text{TiO}_2 + 61\text{Al} + 24\text{Ca} = 2\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + 33\text{TiAl}$	$\text{Ti}_3\text{Al}_5\text{-TiAl}_2\text{-TiAl}_3\text{-Ti}_5\text{Al}_{11}$	$\text{CaAl}_4\text{O}_7\text{-Ca}_3\text{Al}_2\text{O}_6\text{-CaAl}_{12}\text{O}_{19}$	$\text{Al}_2\text{O}_3$
5	$3\text{TiO}_2 + 5\text{Al} + 3\text{Ca} = \text{Ca}_3\text{Al}_2\text{O}_6 + 3\text{TiAl}$	$\text{Ti}_3\text{Al-TiAl}$	$\text{CaAl}_{12}\text{O}_{19}\text{-Ca}_5\text{Al}_2\text{O}_5$	$\text{Al}_4\text{Ca}$

**Table 3.** The product of reaction 4 (Table 2).

Composition of raw materials			Products
TiO <sub>2</sub> (g)	Al(g)	Ca(g)	
210	131	76	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}, \text{CaO}, \text{Ti}_2\text{O}_3, \text{TiO}_2, \text{Ti}_3\text{Al}, \text{Al}, \text{Ti}, \text{Al}_5\text{Ti}_3$
264	165	96	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}, \text{TiO}, \text{TiO}_2, \text{CaO}, \text{Ti}_3\text{Al}, \text{Ti}$
290	181	105	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}, \text{TiO}_2, \text{TiO}, \text{CaO}, \text{Ti}_3\text{Al}, \text{Ti}$
320	200	116	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}, \text{TiO}, \text{Ti}_2\text{O}_3, \text{Ti}_3\text{Al}, \text{Al}_5\text{Ti}_3$
350	218	127	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}, \text{TiO}, \text{Ti}_2\text{O}_3, \text{CaO}, \text{Ti}_3\text{Al}, \text{Ti}$
380	237	138	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}, \text{TiO}, \text{CaO}, \text{Ti}_3\text{Al}, \text{Ti}$

### 3.2. Thermodynamic Considerations

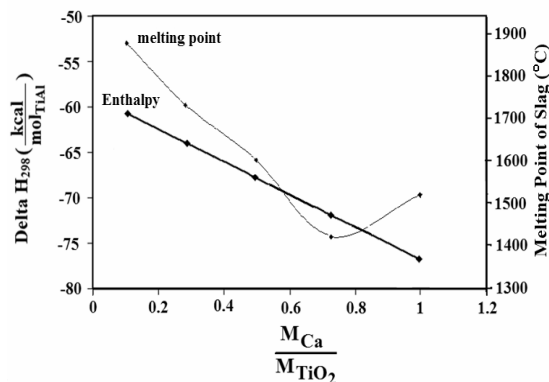
Situation of different calcoaluminates products of reactions (according to table1) in CaO-Al<sub>2</sub>O<sub>3</sub> phase diagram is seen in Fig. 5. According to this figure, melting point of slag is decreased with increasing of CaO/Al<sub>2</sub>O<sub>3</sub> ratio in calcoaluminate products in reactions 1 to 4. Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> compound in reaction 4 has the lowest melting point. But, more increasing of CaO/Al<sub>2</sub>O<sub>3</sub> ratio in slag, leads to increasing of its melting point.



**Fig. 5.** Situation of different calcoaluminate products in CaO-Al<sub>2</sub>O<sub>3</sub> phase diagram.

Enthalpy of different reactions in system of TiO<sub>2</sub>-Al-Ca raw materials at 298K for production of 1 mole of TiAl as well as melting point of calcoaluminat slags versus M<sub>Ca</sub>/M<sub>TiO<sub>2</sub></sub> (M:mole) can be seen in Fig. 6.

According to Fig. 6, increasing of M<sub>Ca</sub>/M<sub>TiO<sub>2</sub></sub> ratio in raw materials leads to increasing of reaction heat and simultaneously decreasing of slag melting point. In M<sub>Ca</sub>/M<sub>TiO<sub>2</sub></sub> equal to 0.727, released heat is enough for partial fusion of slag and metallic product.



**Fig. 6.** Enthalpy of different reactions in TiO<sub>2</sub>-Al-Ca system for production of 1 mole of TiAl as well as melting point of calcoaluminat slags versus M<sub>Ca</sub>/M<sub>TiO<sub>2</sub></sub> (M: mole).

Formation of  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  as a product is due to the partial fusion and therefore partial completion of reaction. But, more increasing of  $M_{\text{Ca}}/M_{\text{TiO}_2}$  ratio led to production of powder products. This is due to the increasing of slag melting point in reaction 5 that prevent its fusion. Therefore holding of released heat and formation of metallic and non-metallic granulates is not possible.

### 3.3. Characterization of Products

After the reaction between  $\text{TiO}_2$ , Al and Ca in all of the reactions in Table 3, the products included a mixture comprising of metallic and non-metallic granulates (Fig. 7). The X-ray diffraction pattern of different granulates indicated in Fig. 7 showed that granulate 1 included some non-metallic phases comprising of  $\text{CaO}$ ,  $\text{C}_{12}\text{A}_7$  ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ),  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$  (Fig. 8). Granulate 2 included  $\text{Ti}_3\text{Al}$ , Al and Ti phases (Fig. 9) whereas granulate 3 included  $\text{Ti}_3\text{Al}$  (Fig. 10) and granulate 4 included Ti,  $\text{Al}_5\text{Ti}_3$ ,  $\text{Al}_2\text{Ti}$  and  $\text{TiSi}$  phases (Fig. 11).

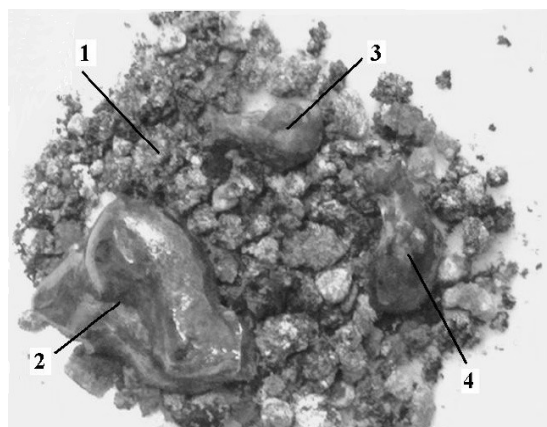


Fig. 7. Products resulted by smelting of  $\text{TiO}_2 - \text{Al} - \text{Ca}$

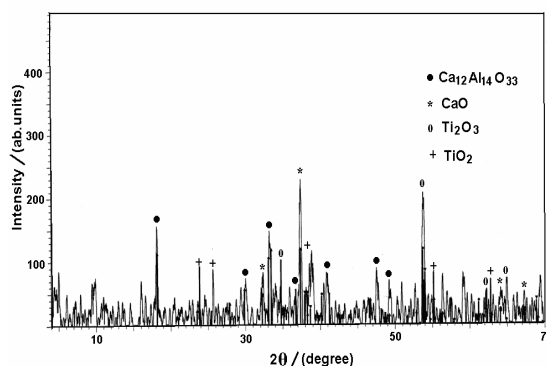


Fig. 8. XRD analysis from granulate 1 of Fig. 7.

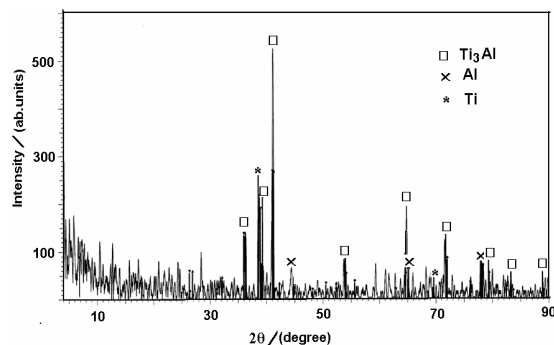


Fig. 9. XRD analysis from granulate 2 of Fig. 7.

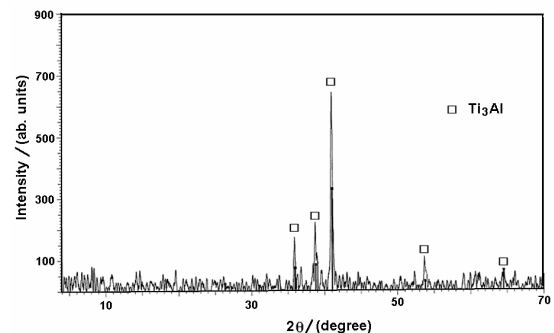


Fig. 10. XRD analysis from granulate 3 of Fig. 7.

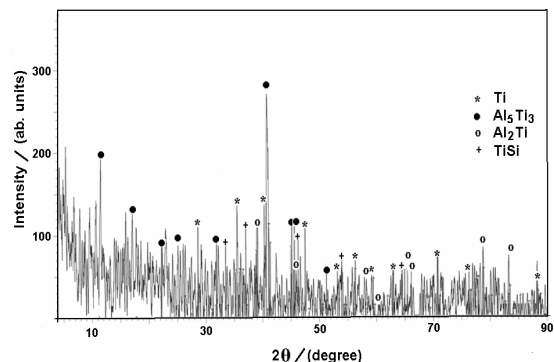


Fig. 11. XRD analysis from granulate 4 of Fig. 7.

#### 3.3.1. Microscopic study of a metallic granulate

Granulate 2 in Fig. 7 is a metallic multi-phases material. Figs. 12 and 13 are the optical and scanning electron microscope microstructure of this granulate, respectively. From the optical microstructure (Fig. 12), it is seen that product contained high amount of porosities. In order to analyse the microstructure, SEM examination was used. The SEM microstructure showed three different regions (Fig. 13). According to EDX analysis, the matrix phase was  $\text{Ti}_3\text{Al}$ . The white precipitation was Ti and the dark precipitation was Al. On the basis of the theoretical reactions (Table 1), it is expected that  $\text{TiAl}$  be presented in

the final product. Lack of TiAl in final product could be due to the fact that during the reactions, the temperature was not high enough and therefore reaction was not completed. The uncompleted reactions result in production of metallic and non-metallic granulates.

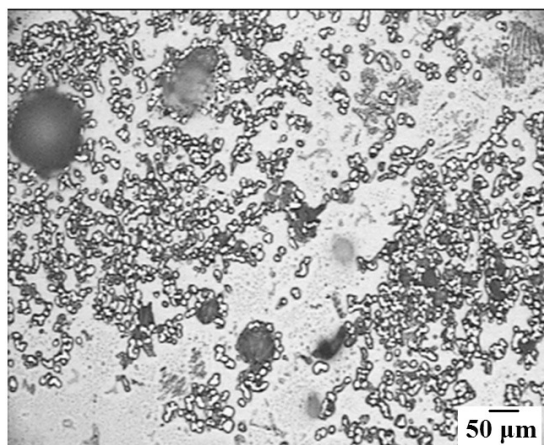
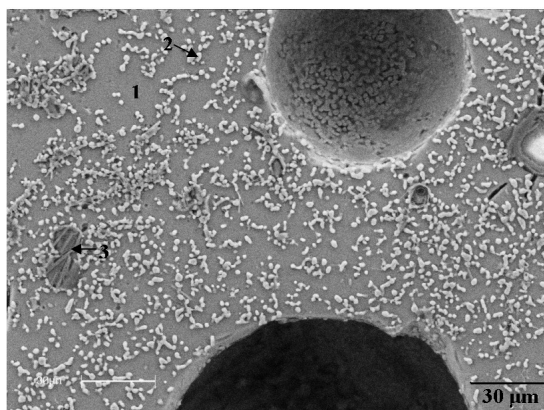


Fig. 12. Optical microstructure of metallic granulate 2 of Fig. 7.



Region analysed	Ti(wt%)	Al(wt%)
1	77.23	22.14
2	95.73	3.13
3	-	99.36

Fig. 13. SEM microstructure of metallic granulate 2 in Fig. 7 and EDX analysis of indicated area. 1= Ti<sub>3</sub>Al, 2=Ti, 3=Al

### 3.4. Remelting of Metallic Granulates

Alumino-calciothermic reduction of TiO<sub>2</sub> according to reaction numbered 4 (Table 1) led to production of metallic and non-metallic granulates. The metallic granulates can be separated easily. 25 g of separated metallic granulates remelted in an arc remelting furnace under high purity argon. Chemical analysis of obtained ingot is shown in table 4. This

composition can be related to TiAl region in phase diagram indicated in figure 1. On the other hand x-ray diffraction pattern of product reveals the formation of TiAl, Ti<sub>3</sub>Al and TiAl<sub>3</sub> phases.

Production of Ti<sub>3</sub>Al and TiAl<sub>3</sub> phases as well as TiAl can be described on the basis of Ti-Al phase diagram. According to figure 1, TiAl is a stable phase in following chemical composition domain:

$$\text{Ti}_x\text{Al}_{1-x} \quad x=44-52 \text{ (atomic percent)}$$

Therefore, if chemical composition of a group of atoms with lattice structure of TiAl changes from Ti<sub>50</sub>Al<sub>50</sub> to Ti<sub>52</sub>Al<sub>48</sub>, it is possible to formation of two unites with lattice structure of TiAl<sub>3</sub> for keeping of elemental equilibrium. On the other hand, if chemical composition of a group of atoms with lattice structure of TiAl changes from Ti<sub>50</sub>Al<sub>50</sub> to Ti<sub>48</sub>Al<sub>52</sub>, it is possible to formation of two unites with lattice structure of Ti<sub>3</sub>Al.

Table 4. Chemical analysis of remelted ingot

Element	Ti	Al	Ca	Others
Weight Percent	48.59	51.14	0.12	0.15

## 4. CONCLUSIONS

A non-completed reaction between TiO<sub>2</sub>, Al and Ca, according to considered reaction of  $33\text{TiO}_2 + 61\text{Al} + 24\text{Ca} = 2\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + 33\text{TiAl}$  resulted in the formation of a mixture of metallic granulates consisting of Ti<sub>3</sub>Al, Ti, Al<sub>5</sub>Ti<sub>3</sub>, Al<sub>2</sub>Ti and non-metallic granulates consisting of CaO, C<sub>12</sub>A<sub>7</sub> (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>), Ti<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The metallic granulate contained high amount of porosities. Remelting of the metallic granulates led to obtain an ingot consisting of TiAl, Ti<sub>3</sub>Al and TiAl<sub>3</sub> phases.

## REFERENCES

1. S. Djanarthany, J. C. Viala and J. Bouin: Materials chemistry and physics, 2001, 72,301.
2. D. M. Dimiduk: Materials Science and Engineering, 1999, A263, 281.
3. E. A. Loria: Intermetallic, 2002, 9,997.
4. C. M. Austin: Current Opinion in Solid State and Materials Science, 1999, 4,239.
5. P. A. Bartolotta and D. L. Krause: NASA/TM, 1999, 209071.
6. H. Kestler and H. Clemens: Titanium and titanium alloys, 1nd edn, edited by C. Leyens and M. Peters, Wiley-VCH

- GmbH&Co. KGA, Germany, 2003, 360-361.
7. O. M. N. D. Teodoro, J. Barbosa, M. Duarte and A. M. C. Moutinho: *Applied Surface Science*, 2004, 231-232, 854.
  8. J. Guo, Y. Liu, Y. Su, H. ding, G. Liu and J. Jia: *Metallurgical and Materials Transactions B*, 2000, 31B, 837.
  9. A. D. Ryabtsev, A. A. Troyansky and O. V. Tarlov: *problem of SEM*, 2000, No. C. 75, 78.
  10. J. H. Moll: *JOM*, May 2000, 55.
  11. S. J. Hales and P. Vasquez: in *Proc. symp. On Gamma Titanium Aluminides*, TMS, eds Kim, Clemens, Rosenberger, Hampton, USA, 2003.
  12. K. Uenishi, T. Matsubara and K. F. Kobayashi: *Scriptamater*, 2001,44,2093.
  13. F. H. Froes and R. M. German: *Metal Powder Report*, 2000, 55 ,6, 12.
  14. N. Bertolino, M. Monagheddu, A. Tacca, P. Giuliani and C. Zanotti: *Intermetallics*, 2003, 11, 41.
  15. A. Biswas: *Acta Materialia*, 2005, 53, 1415.
  16. N. Travitzky, I. Gotman and N.Claussen: *Materials Letters*, 2003, 57, 3422.
  17. Run-hua Fan, Bing Liu, Jing-de Zang, Jian-qiang Bi and Yan-sheng Yin: *Materials Chemistry and Physics*, 2005, 91,140.
  18. Z. W. Li, W. Gao, D. L. Zhang and Z. H. Cai: *Corrosion Science*, 2004, 46, 1997.
  19. A. Kamali, H. Razavizadeh and S. M. M. Hadavi: *AU Patent*, 2005, 2005100278 B4.
  20. S. C. Carniglia, S. C. and G. L. Barna: *Handbook of industrial refractories technology. Principles, types, properties and application*, Park Ridge, USA, 1992, 627.
  21. D. M.Beal, S.G.Lakhwani and L.R.Pinckney: *US Patent*, 2004, 6689707 B1.
  22. R. C. Devries, R. Roy and E. F. Osborn: *J. Phys. Chem.* 1954,58,1072.
  23. S. Jonas and F. Nadachowski: *Ceramic International*, 1998, 24,211.
  24. S. Jonas, F. Nadachowski and D. Szwagierczak: *Ceramics International*, 1999, 25, 77.
  25. J. S. Lee, C. K. Hsu and K. S. Jaw: *Thermochemica Acta*, 2001, 367-368, 381.
  26. U. A. Tamburini, F. Maglia, G. Spinoio and Z. A. Munir: *Chemica & Industria*, 2000, Dicembre.
  27. A. Duarte, F. Viana and H. M. C. M. Santos: *Materials Research*, 1999, 2, 3, 191.