

**SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS
OF FERRO SILICO TITANIUM**

K. R. Shaymardanov, I. M. Shatokhin, I. R. Manashev

NTPF Etalon Ltd, 455030, Zapadnoe shosse, 15, Magnitogorsk, Russia, mail@ntpf-etalon.ru

ABSTRACT

Results of self-sustaining combustion process in the titanium-ferrosilicon system investigations are presented. These data was used for developing of experimental-industrial technology of production ferro silico titanium with high titanium content for steel alloying.

KEYWORDS: *Ferro silico titanium, ferrotitanium, titanium, titanium-containing steel, self-propagating high-temperature synthesis, combustion.*

At present, titanium is actively used for alloying of wide assortment of steels thanks to its specific properties. Titanium is used for modern HSLA-steels, pipe-steels, stainless steels and others. Mainly, the mechanism of it influence on the steel quality is associated with formation of titanium carbides, nitrides and carbonitrides in the steel.

For steel alloying ferrotitanium is used usually. Depending on the method of production, ferrotitanium can be with high (~70 % Ti) and low (≤ 40 % Ti) titanium content. High-grade ferrotitanium is usually obtained by melting titanium-containing waste in induction furnaces. Low-grade ferrotitanium is produced by recovery from ilmenite in special melting aggregates. Ilmenite concentrate, iron ore, aluminum powder, ferrosilicon and lime are used as raw materials. Sometimes, when high-purity steel grades are produced, vacuum-melted ferrotitanium is used. Standard ferrotitanium contains considerable amount of impurities (such as non-ferrous metals, nitrogen, oxygen, hydrogen, carbon, sulfur, phosphorus), which come to alloy from raw materials and atmosphere during production. Moreover, assimilation degree of titanium from ferrotitanium remains low.

That is why full or partial replacement of ferrotitanium by alternative titanium containing alloys is actual. This problem can be solved by creating of complex master-alloys, which contain titanium as basic element and high-level elements, such as Si, Al, Ca, etc. It is supposed, that these elements will protect titanium against oxidation, because they are strong deoxidizers. In this way, titanium assimilation will be higher. Thus, to be most effective, new alloy should to meet following requirements:

- high titanium content;
- low impurities content;
- presence of elements with high affinity to oxygen.

This alloy will give high and stable titanium assimilation, will allow to produce steels with narrow titanium limits and will reduce impurities content in metal. The most economical alternative to ferrotitanium can be ferro silico titanium. Usually ferro silico titanium is obtained by melting titanium, metallic silicon and low-carbon steel in induction furnace or by recovery from ilmenite ore. But it is impossible to produce ferro silico titanium with high titanium content (more than 30 % Ti) by furnace methods, because of high melting point of titanium silicides and strong liquation during crystallization. Moreover, alloy, obtained by furnace methods, have higher concentration of nitrogen, oxygen and hydrogen, which penetrate into the melt from the atmosphere. So it is important to use fundamentally different method of titanium ferrosilicide obtaining, that allow to obtain high recovery of product with low impurities content with lowest costs of electricity. Such

method is self-propagating high-temperature synthesis (SHS). When SHS is applied, no traditional furnaces are used. The process is carried out in special SHS-reactors at the atmosphere of inert gas or vacuum. At the combustion synthesis, as well as at the traditional metallothermic process, energy source is the heat of chemical reactions. But unlike metallothermy, SHS is slagless.

The Ti-Si system has 5 silicides: TiSi, TiSi₂, Ti₅Si₃, Ti₃Si₄ и Ti₃Si. Ti₅Si₃ has highest melting point. Physical and chemical properties of titanium silicides are presented at table 1. Formation of titanium silicides occurs with great heat release, so that adiabatic combustion temperature is high. Regularities of interaction of titanium and silicon are studied in detail at works [3, 4]. It was shown, that the combustion in a powder compound of titanium and silicon can be implemented in a wide range of parameters changing such as the components ratio, powders dispersion, etc. It can be expected, that heat release during chemical interaction in ternary system Ti-Si-Fe will be enough to carry out the process in self-propagating mode.

Table 1: Physical and chemical properties of titanium silicides [5]

Characteristics	Ti ₅ Si ₃	TiSi	TiSi ₂	Ti ₃ Si ₄	Ti ₃ Si
The heat formation, kJ/mol	581,2	132,8	136,6	—	—
The temperature of crystallization, °K	2120	1760	1540	1920	1170
Density, g/cm ³	4,3	4,03	4,21	—	—
Adiabatic combustion temperature, °K	2500	2000	1800	—	—

It is known, that high exothermicity of raw materials interaction is an essential condition for all SHS-reactions. To determine the possibility of self-propagating process, calculation of adiabatic temperature in ternary system Ti-Si-Fe with an iron content of 0 to 90 % was carried out using thermodynamic data and methodology, represented at [5]. During calculation it was assumed, that iron does not took part in the reaction and combustion products are titanium silicide Ti₅Si₃ and α-iron:



Combustion temperature was calculated using following formula:

$$(1 - \mu) \cdot \Delta H_{Ti_5Si_3}^{T_{ad}} + \mu \cdot \Delta H_{Fe}^{T_{ad}} = (1 - \mu) \cdot (Q - \nu_{Ti_5Si_3} \cdot L_{Ti_5Si_3}) \quad (2)$$

where: $L_{Ti_5Si_3}$, $\nu_{Ti_5Si_3}$ – respectively the heat and the degree of fusion of Ti₅Si₃; $\Delta H_{Ti_5Si_3}^{T_{ad}}$ и $\Delta H_{Fe}^{T_{ad}}$ – change of enthalpy of titanium silicide formation and iron when temperature increases from T₀ to T_{ad}; μ – amount of iron in the combustion products.

The results of calculation are presented on figure 1. It is a curve of relationship between adiabatic temperature of combustion of (5Ti + 3Si)-Fe-compound and concentration of iron in it.

The results show, that adiabatic temperature remains enough high despite reduction of heat effect when iron is added to (5Ti + 3Si)-compound (more than 2000°K when iron concentration is changed between 0 and 50 %). Therefore, we can expect, that process can be carried out in self-propagating mode in wide range of Ti, Si, Fe concentration.

To carry out the researches, laboratory SHS-reactor with 20 liters volume was constructed. This plant allows to carry out researches of SHS-processes in wide range of pressure: from 0,01 to 10 MPa. Ti-Si-Fe-system is qualified as SHS-gas-free system, that is all raw materials and products are in condensed state. There is no relationship between combustion parameters and pressure and this is the distinction of these systems. Relationships between combustion rate, combustion

temperature, ratio of raw components and particle size of titanium powder in titanium-ferrosilicon system were investigated using laboratory SHS-reactor.

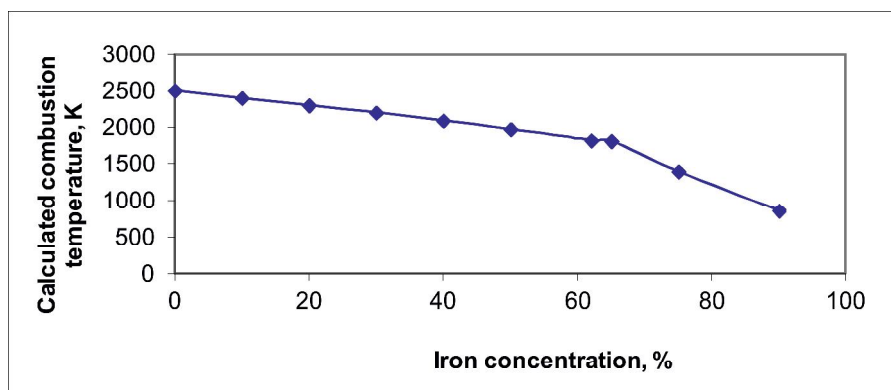


Figure 1: Influence of iron concentration on adiabatic temperature of combustion of $(5\text{Ti} + 3\text{Si})\text{-Fe}$ -compound

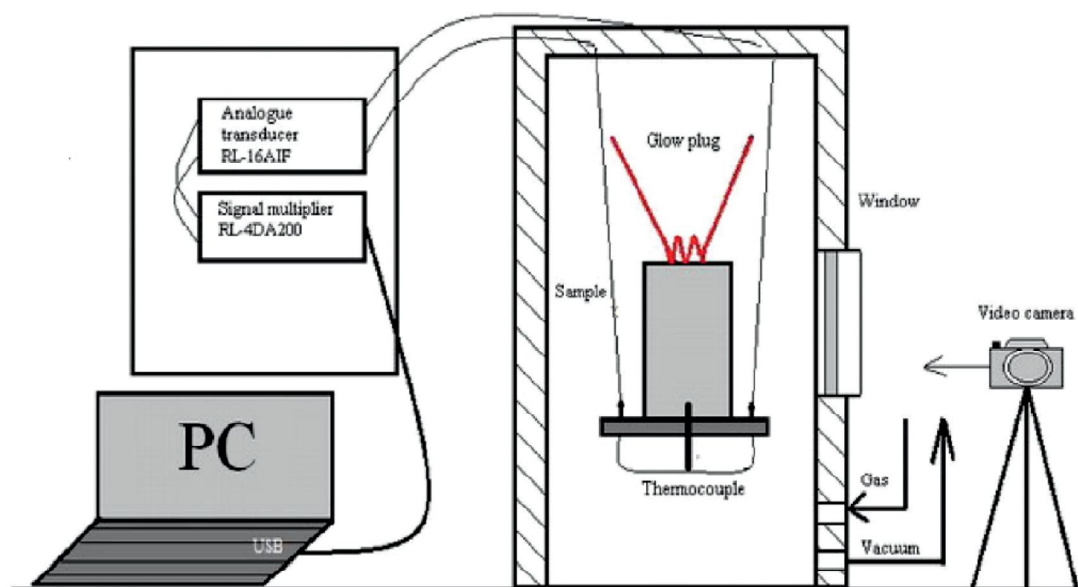


Figure 2: Laboratory SHS reactor scheme

Porous titanium powder TPP-4 TU 1791-449-05785388-99 produced by JSC “VSMPO-AVISMA Corporation” and ferrosilicon powder FeSi75 GOST 1415-93 produced by JSC “Chelyabinsk Electrometallurgical Integrated Plant” are used as raw materials. Temperature was measured by thermocouple method using tungsten-rhenium thermocouples TR-5/TR-20, analogue transducer RL-16AIF and signal multiplier RL-4DA200. Combustion rate was measured by video camera.

Combustion rate and temperature are basic parameters of SHS-method. These parameters determine process productivity and safety, as well as requirements to equipment. It is known, that modes and possibility of SHS depend on many factors. Most important factors, except high exothermicity, are raw components ratio and powder particle size.

In general, combustion synthesis in Ti-Si-Fe-system can be implemented using different

schemes: Ti + Si + Fe; Ti + FeSi + Fe; Ti + FeSi; FeTi + Si + Fe; FeTi + Si and others. In this work process in titanium-ferrosilicon system is investigated.

Combustion synthesis in this system was carried out in a wide range of raw components ratio (figure 3 and 4). As a result of combustion product with 60-75 % Ti and 18-27 % Si is formed. Figure 3 shows relationship between combustion temperature and titanium/ferrosilicon ration in the mixture.

As we see, combustion temperature depends weakly on components ratio and remains almost constant in a wide range of raw components ratio ($1720 \pm 50^\circ\text{K}$). We think it happens because changing of raw components ratio in studied ranges affects just on proportion of the liquid phase in products, but temperature of forming melted products that is close to measured temperature, remains constant.

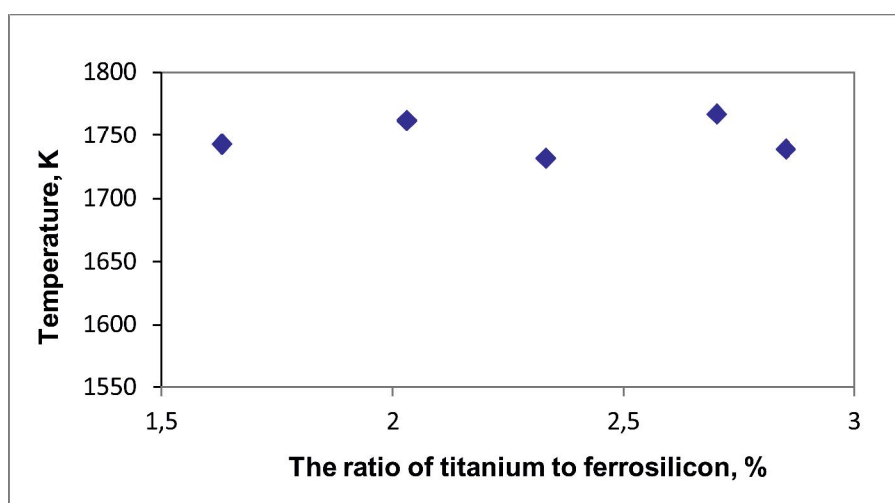


Figure 3: Relationship between combustion temperature and components ratio

Figure 4 shows relationship between combustion rate and components ratio of (5Ti + 3Si)-Fe-compound.

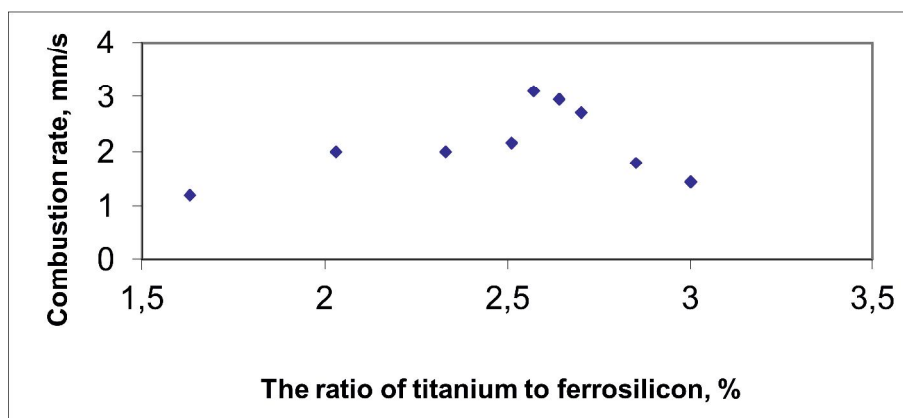


Figure 4: Relationship between combustion rate and components ratio

We can see from the figure, that combustion rate reduces both when titanium concentration increases and when it reduces. Maximum combustion rate was obtained on the compound with 72 % Ti.

Figure 5 shows relationship between combustion temperature and titanium powder particle

size when component ratio provides formation of Ti_5Si_3 .

The figure shows that temperature stays about the same level ($1720 \pm 50^\circ K$) and changes weakly when titanium powder particle size is varied.

The next figure presents relationship between combustion rate and titanium powder particle size (figure 6). This figure tells, that combustion rate changes weakly ($2 \text{ mm/s} \pm 0,25 \text{ mm/s}$) when titanium powder particle size is varied. Figures 5 and 6 tell us, that combustion in this system can be carried out in wide range of titanium powder particle size and combustion temperature with almost constant rate.

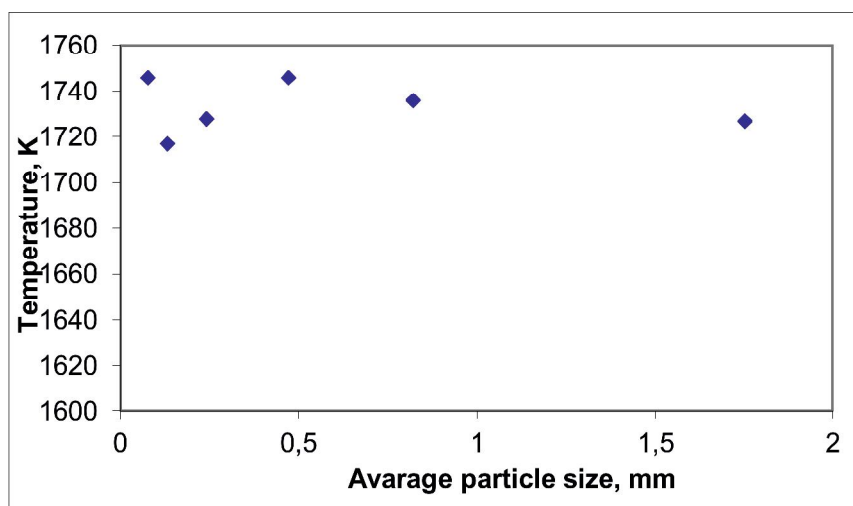


Figure 5: Relationship between combustion temperature compound and titanium powder particle size in titanium-ferrosilicon compound

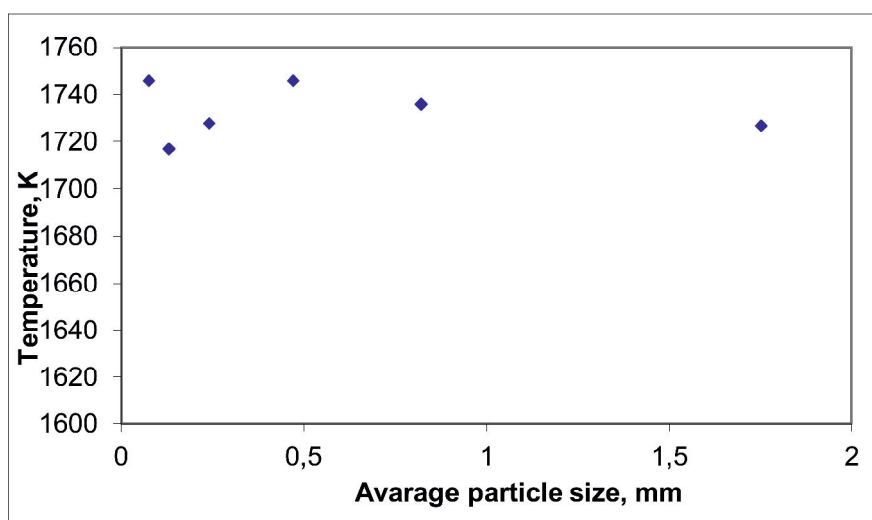


Figure 6: Relationship between combustion rate and titanium powder particle size in titanium-ferrosilicon system

Thus, these investigations have shown that SHS-technology can be applied to obtain ferro silico titanium with high titanium content. It is possible to obtain alloys with various titanium content and various densities by varying of initial mixture and particle size of initial powders. Moreover, lack of waste and electricity consumption will bring low cost and provide high competitiveness of products. At the same time producing of new alloy in inert gas atmosphere will

increase the purity of end product.

Investigations results were used for developing of experimental-industrial technology of ferro silico titanium production by SHS-method. Specifications for optimal SHS-ferro silico titanium composition are developed (table 2).

Table 2: Chemical composition of SHS-ferro silico titanium

Grade	Ti	Si	C	S	P	O	N	H
			max					
FST 70	61-74	18-27	0,15	0,005	0,009	0,1	0,05	0,005

3. CONCLUSIONS

The process of obtaining of ferro silico titanium with high titanium content (to 75 %) by self-propagating high-temperature synthesis was investigated. Relationships between combustion rate, combustion temperature and initial components ratio, titanium powder particle size were received. As it turned out, temperature depends weakly on initial components ratio and titanium powder particle size and remains at the same level (about $1720 \pm 50^\circ\text{K}$). Combustion rate is also weakly depends on titanium powder particle size, but we can see, that combustion rate reduces both when titanium content increases and reduces. Maximum combustion rate was obtained on the compound with 72 % titanium. Based on these data, experimental-industrial technology of obtaining of ferro silico titanium by SHS-method was developed.

4. REFERENCES

- [1] Lyakishev N.P., Pliner, U.L., Lappo S.I. Alloys and alloying steel with titanium. M.: Metallurgiya, 1985. 230 p.
- [2] Gasik M.I. Theory and technology of production of ferroalloys. M.: Metallurgiya, 1988. 340 p.
- [3] Sarkisyan A.R. Some laws of combustion of mixtures of transition metals with silicon and silicide synthesis // Physics of combustion and explosion. 1977. № 3. pp. 34-40.
- [4] Azatyan T.S. Some laws of combustion of titanium with silicon // Physics of combustion and explosion. 1978. № 1. pp. 44-49.
- [5] Novikov N.P., Borovinskaya I.P., Merzhanov A.G. Thermodynamic analysis of self-propagating high-temperature synthesis reactions // Combustion Processes in Chemical Technology and Metallurgy: Proceedings / Ed. A.G. Merzhanov. Chernogolovka, 1975. pp. 174-188.