Application of Titanium Sponge Screenings for Obtaining Titanium Carbide and Carbidic Steel

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ANNOTATION

The technology of titanium carbide production by a selft-propagation high-temperature synthesis (SHS method) from TG-Tv titanium sponge screenings with particle sizes of –0.45+0.08 mm and –0.18+0.08 mm subjected to a special treatment in order to improve their quality and fire-and explosion-safety has been developed and tested on pilot scale.
The process flow diagram uses a novel reactor design which enables the charge burning at reduced pressure and temperature, with the removal of reaction gases.
Titanium carbide obtained meets, by its composition and properties, the requirements to the commercial-grade titanium carbide powder, %(mass): C_{bound}-18.40; C_{free}-0.85; oxygen – 0.38; hydrogen – 0.003; nitrogen – 0.03; titanium-balance. With this, the good-to-bad ratio was 95.5-97.8%.
Pilot samples of carbidic steel 6X6B3MΦC + 25% TiC produced using titanium carbide have good physical and mechanical properties, and minimum porosity. The samples are practically free of defects associated with oxide films.

Key words: TG-Tv screenings, pneumatic classification, titanium carbide, SHS-method, carbidic steel, 6X6B3MΦC + 25% TiC.

1.EFFECT OF ADDITIONAL TREATMENT OF TG-TV TITANIUM SPONGE SCREENINGS ON THEIR QUALITY AND FIRE-AND EXPLOSION-SAFETY

TG-Tv rejects are formed during the processing of titanium sponge due to some salient features of the process for titanium reduction with magnesium and the conditions of processing the metal produced into a marketable product. This grade consists of those portions of titanium sponge formed in the reactor which are contaminated with impurities entering with the raw material and from the reactor steel walls.

The grade is typically composed of the following portions of the sponge block:

- bottom low-grade end of the block cut off because of excessive concentration of impurities; parts of the block cut from its side surface, from the reactor cover, walls and false bottom and heavily contaminated with iron;
- fine fractions of titanium sponge scull portion (-5 or –12 mm) and bar portion (-2mm) which are embrittled through excessive concentration of iron, nitrogen, oxygen, chlorine, nickel and hydrogen.

These rejects are delivered to titanium powder producers. There, the coarse lumps are comminuted, screened, averaged, etc. In doing so, the screenings of –0.45 and -0.18 mm size are formed with a high concentration of impurities which, in the recent past, prohibited their application for the production of titanium carbide. It is also important than the screenings present fire- and explosion-hazard, and they cannot be used unless a technology of their surface treatment is developed.

Fire- and explosion-safety of screenings is also a matter of economy. The application of too sophisticated treatment processes and the use of explosion-proof-equipment leads to a substantial increase in the production costs both of powders and products of them. This can make the application of powdered screenings in some industries inexpedient. For this reason, all methods of improving the quality of screening shall be aimed at settling this point. By one of the methods, the quality of powders can be improved by the separation of finely dispersed contaminated portion from the bulk of the metal.

Wet screening of metal on vibrating sieves used in the industry today does not permit the contaminated product to be separated for the following reasons:

a) spongy branching shape of screening particles will allow them to remain on a sieve with a mesh size larger than their cross-section and pass through a sieve with a mesh size smaller than their length;

b) – 0.45 mm screenings contain up to 10% of particles larger than the normal ones and up to 15% of particles smaller than 0.08 mm, difficult to pass through the sieve meshes. Special means to rub the particle through the sieve are not allowed for the risk of titanium ignition from sparks of electrostatic origin.

The sieves with a mesh size smaller than 0.04 mm are extremely difficult to manufacture. Now in use are the methods of producing sieves by the treatment of metal plates, by etching or by electric arc method. By these methods, geometrically perfect holes of 0.005 mm can be obtained but, for their high cost, such sieves can find application only on laboratory scale but not for commercial-scale production of powders.

This paper presents the results of investigation into the possibility of improving the quality of – 0.45 and – 0.18 mm TG-Tv screenings by the removal of heavily contaminated portion with a particle size of less than 0.08 mm from the bulk of the metal and reducing fire and explosion risk by a surface treatment.

The following screenings were tested:

a) – 0.18 mm TG-Tv titanium sponge screenings with the following concentration of impurities, %(mass): iron – 1.80; chlorine – 0.12; nitrogen – 0.20; hydrogen – 0.90; oxygen – 0.45.

Lower concentration limit of flame propagation (LCLP) was 100 g/m^3, autoignition temperature (t_c) was 673 K.

b) – 0.45 mm TG-Tv titanium sponge screenings with the following concentration of impurities, %(mass): iron – 1.00; chlorine – 0.10; nitrogen – 0.12; hydrogen – 0.60; oxygen – 0.35.

LCLP = 200g/m^3, t_c = 803 K.

To improve fire-and explosion-safety of the screenings, they were additionally treated with a 5% solution of magnesium, sodium and potassium chlorides in a ratio of 1 : 4 : 5 or with a 5% solution of spent electrolyte from magnesium production.

Relative reduction in the fire or explosion risk was estimated by the values of LCLP and t_c determined in accord with GOST 12.1.044-89.

Heavily contaminated portion with particles smaller than 0.08 mm was separated from the bulk of the metal by pneumatic classification using a special-purpose pneumatic classificator for – 0.45 mm particles and a VCK-9 unit for – 0.18 mm particles.

Additional treatment of the screenings with magnesium chloride, sodium chloride and potassium chloride solutions resulted in the increase in the LCLP from 100 g/m^3 up to 300 g/m^3 for – 0.18 mm screenings, and from 200 g/m^3 up to 400 g/m^3 for – 0.45 mm screenings. With this, the autoignition temperature for – 0.18 mm particles rose from 673 K to 758 K, for – 0.45 mm particles – from 803 K to 823 K.

Absolute values of LCLP and t_c are the evidence of actual fire- and explosion-safety of processed screenings which can be subjected to pneumatic classification.

After pneumatic classification of – 0.18 mm screening using VCK-9 unit, the content of - 0.08 mm fraction reduced from 25.0 to 7.5%(mass), while the classification using a special-purpose pneumatic classificator resulted in the reduction to 2.5%(mass). Total content of impurities reduced from 3.85% to 2.76%(mass) when classified using the VCK-9 unit and to 2.5%(mass) after the special-purpose classificator.

Processing of – 0.45 mm screenings in the special-purpose classificator resulted in the reduction in the content of - 0.08 mm particles from 15.0% to 3.0%(mass), while the total content of impurities reduced from 2.37 to 1.5%(mass).

Along with the improvement of screenings quality, they become more fire-and explosion-safe due to the removal of – 0.08 mm particles.

In parallel, the screenings were classified into narrow fractions to make a charge with pre-set properties which increased the efficiency of reaction between the charge components during the SHS and the yield of good product.

Shape and sizes of - 0.18 and – 0.45 mm screenings were studied before and after classification as they are critical for SH-synthesis [1]. The more branched is the structure of particles, the larger is the surface of carbon and metal contact. This makes the interaction of charge components more efficient resulting in a higher yield of good product.

By pneumatic classification, metal and non-metal mechanical impurities were removed from the bulk of the metal, and thus the quality of screenings was improved. The impurities entering the carbide and then the articles of carbidic steel led to the formation of various voids and defects.

Based on the results of the study, a schematic process flow diagram can be proposed for the preparation of – 0.18 mm and – 0.45 mm TG-Tv screenings for titanium carbide production (Fig.1.1).

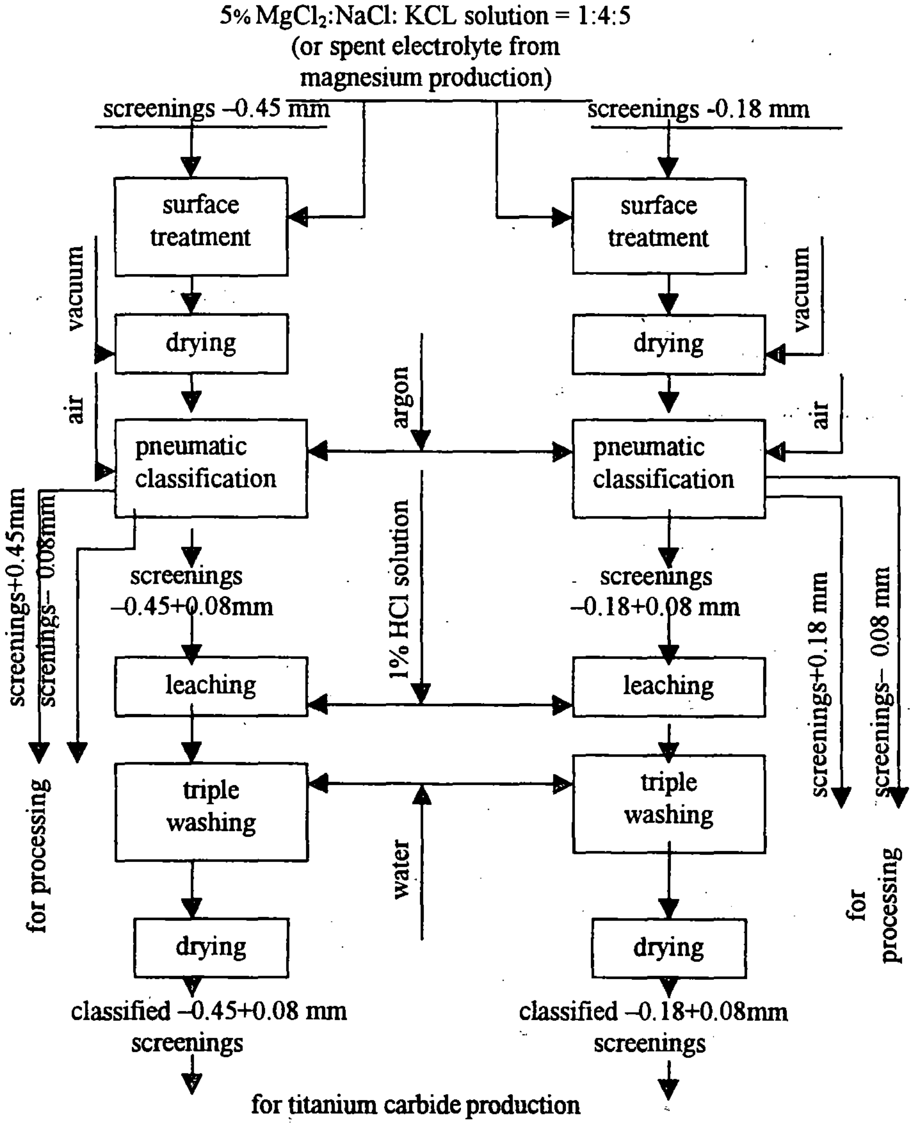

Fig. 1.1. Flow diagram of preparing –0.45 mm and –0.18 mm TG-Tv screenings for titanium carbide production

The flowsheet provides for the application of standard equipment in wide use in the powder metallurgy, while, for the surface treatment of screenings, cheap, easily available, non-contaminating potassium, sodium, magnesium chlorides or spent electrolytes from magnesium production are used. On pilot scale, a lot of - 0.18 + 0.08 mm and – 0.45+0.08 mm screenings was produced containing less than 2%(mass) of impurities suitable for the production of titanium carbide by the SHS-method.

2.STUDY INTO THE PROCESS FOR TITANIUM CARBIDE PRODUCTION BY THE SHS-METHOD FROM TG-TV TITANIUM SPONGE SCREENINGS

Recently, the production of titanium carbide has encountered a problem with raw materials connected with the deficiency of titanium dioxide and TG-ShM titanium sponge. Research work was carried out to involve low-grade TG-Tv titanium sponge in the production of titanium carbide. Titanium sponge was milled and classified into fractions to obtain titanium powders of quality sufficient for their application in the production of titanium carbide. By the above method, titanium sponge screenings with a particle size of – 0.45 and – 0.18 mm are formed which could not be used for titanium carbide production due to excessive concentration of impurities and non-availability of the process for their removal.

This paper presents the results of investigation into the effect of – 0.18 and – 0.45 mm TG-Tv screenings on the properties of titanium carbide produced by the self-propagating high-temperature synthesis [2].

The following materials were tested:

a) – 0.18 mm and – 0.45 mm TG-Tv screenings and the mixture of these fractions in a ratio of 1 : 1 after the removal of the most contaminated portion (- 0.08 mm);
b) commercial-grade carbon of PM 15 GS grade per GOST 7885-87 E.

Burning of charge based on TG-Tv screenings was carried out in the reactor SHS-100 designed for the self-propagating high-temperature synthesis with a removal of reaction gases in the stream of argon at a pressure of not more than $1.5 \cdot 10^5$ Pa.

As required by the reactor SHS-100 design, the charge was first compacted in a shell of graphitized fabric TGN-2M, and then placed in the reactor. Between the reactor wall and the shell, a backfill was provided of final product rejects for heat insulation and removal of gases.

Burning over, the reactor was sealed, filled with argon, and the final product cake was cooled down. Upon the removal of sealing, the shell of graphitized fabric was easily separated from the backfill together with titanium carbide formed by synthesis.

Carbide cake was ground in a hard-alloy mill using a standard technology. Particles of – 0.25 mm size were screened off from the bulk of the powder. This particle size properties were characteristic for the whole material but not for its individual fractions.

The influence of the quality of screenings on the properties and yield of good titanium carbide of – 0.25 mm particle size was investigated.

Test results are given in Table 2.1.

Table 2.1

Influence of the quality of TG-Tv screenings on the properties of titanium carbide of – 0.25 mm particle size

Material	TG-Tv screenings						Titanium carbide				Good-to-bad ratio,%
	Mass fraction of impurities, %						Content of components, %(mass)				
	Fe	Cl	N	H	O	total	C_{free}	C_{bound}	O	total	
-0.18 mm screenings prior to pneumatic classification: (+0.18 mm content –10%, -0.08 mm content – 25%)	1.80	0.12	0.20	0.90	0.45	3.85	1.40	17.00	0.80	2.82	91.0
After classification: (+0.18 mm content – 2.5%, -0.08 mm content – 7.5%)	1.30	0.09	0.12	0.65	0.40	2.76	1.20	18.00	0.42	1.98	94.5
-0.45 mm screenings prior to classification: (+0.45 mm content – 10%, -0.08 mm content – 15%)	1.00	0.10	0.12	0.60	0.35	2.37	1.15	17.60	0.60	2.08	93.5
After classification: (+0.45 mm content – 0.5%, -0.08 mm content – 3.0%)	0.65	0.08	0.12	0.40	0.30	1.55	1.05	18.25	0.40	1.65	95.6
Classified screenings with –0.18 mm and – 0.45 mm particle size in a ratio of 1:1	0.90	0.08	0.10	0.40	0.35	2.05	0.85	18.40	0.38	1.80	97.8

It is evident that the chemical composition of titanium carbide and its yield are a strong function of the screenings quality.

After pneumatic classification, - 0.18 mm screenings have 1.4 times less impurities. The content of bound carbon in the carbide increased from 17.0 to 18.0%(mass). With this, the content of oxygen in the carbide become one-haft as large, and the total quantity of impurities become 1.4 times lower. The good-to-bad ratio increased from 91.0 to 94.5%.

A similar improvement in titanium carbide quality is observed in case where– 0.45 mm classified screenings are used. The good-to-bad ratio increases from 94.5 to 95.6% while a total content of impurities decreases from 2.08 to 1.65%(mass).

Best results as for the quality and the yield of good product were obtained when the mix of classified – 0.45 and – 0.18 mm screenings was used in a ratio of 1 : 1. With this, the lowest total concentration of impurities in the screenings (2.05% mass) and a high yield of good product were achieved (to 97.8%).

The total concentration of impurities in the screenings has the strongest impact on titanium carbide quality. High total concentration of impurities leads to energetic burning, with extensive release of gases into the atmosphere, while the pressure in the reactor rises to $1.8 \cdot 10^5$ Pa. With this, the contact between the charge particles is disturbed, the efficiency of components interaction decreases resulting in a reduced yield of good carbide and a poorer quality of the product.

Pneumatic classification of the screenings improved the conditions of synthesis so that the yield of good product and the content of bound carbon increased. With this, the total content of impurities in carbide did not exceed 2%(mass). Burning was quiet and smooth, free of scattering.

The application of classified – 0.18 + 0.08 and – 0.45 + 0.08 mm screenings in a ratio of 1 : 1 has weakened the impact of charge structure (inner non-uniformity) on the SHS-process. Spongy branching surface of screenings improves the contact between the particles of metal and carbon and the efficiency of initial agents conversion into titanium carbide. Total concentration of impurities in the carbide does not exceed 2%(mass), the good-to-bad ratio is 97.8% and free carbon content is less than 1%(mass).

Based on test results, the process flow diagram of titanium carbide production was elaborated. It is given in Fig.2.1 below.

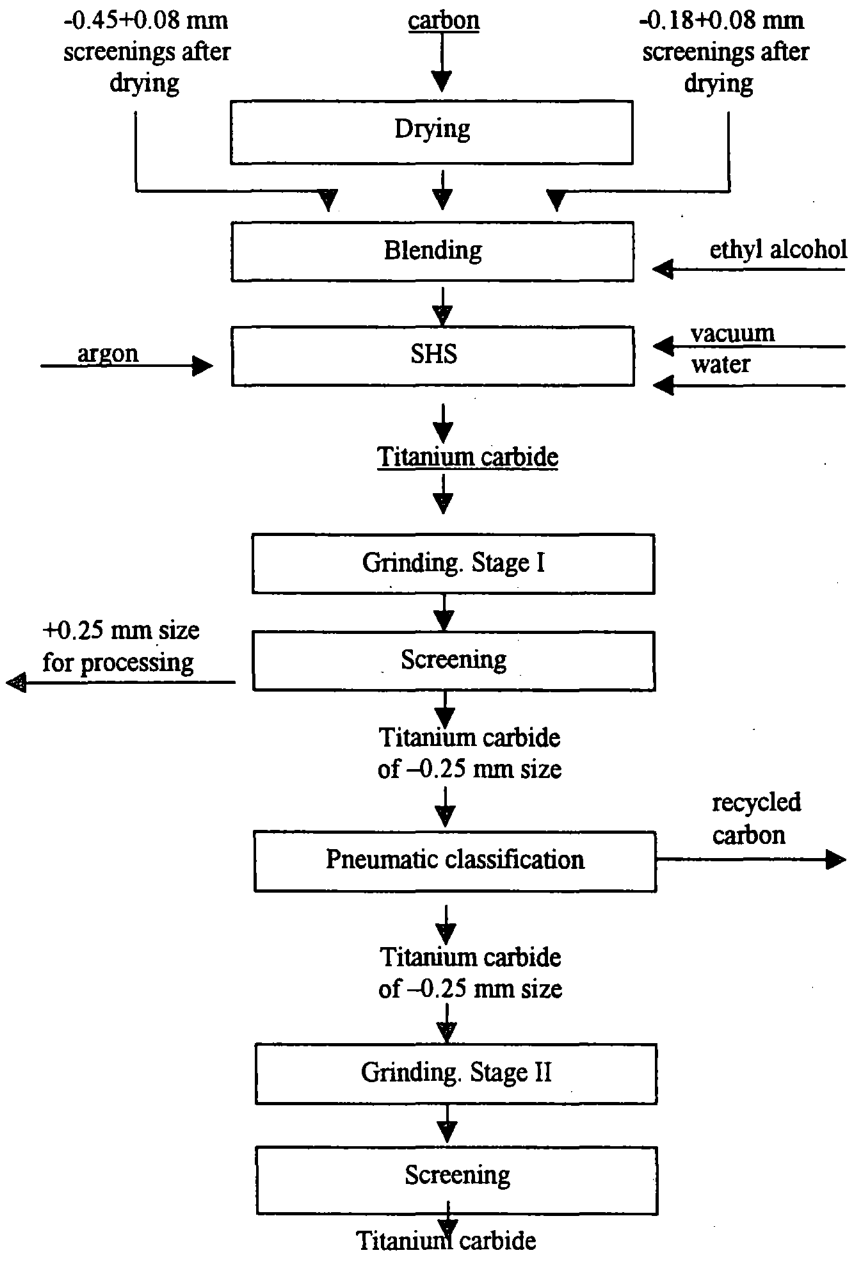

Fig.2.1. Flow diagram of titanium carbide production from –0.45+0.08 mm and –0.18+0.08 mm TG-Tv screenings

Dry commercial-grade carbon and classified titanium sponge screenings are mixed in a ball mill in the atmosphere of ethyl alcohol during $7.2 \cdot 10^4$ s with a ball-to-charge ratio of 2 : 1. The mix is then dried in a vacuum drying oven at a temperature of 373 K during $7.2 \cdot 10^3$ s and transferred warm to the SHS reactor.

Synthesis over, the titanium carbide cake is cooled down together with the reactor during $1.8 \cdot 10^4$ s. Then the carbide cake is discharged and processed using first a hydraulic press, then a jaw crusher and a hard-alloy vibrating mill where the carbide is milled in the atmosphere of ethyl alcohol during $2.88 \cdot 10^4$ s with a ball-to-carbide ratio of 3 : 1.

The product is screened using vibrating screens with a mesh size N 025. Titanium carbide with a particle size of + 0.25 mm is recycled for additional grinding while – 0.25 mm particles are subjected to pneumatic classification to remove free carbon and finest particles of titanium carbide heavily contaminated with impurities.

When purified, titanium carbide is finally comminuted in accordance with the technology described above during $(2.88...7.2) \cdot 10^4$ s depending on the client's requirements.

The process flowsheet of titanium carbide production from classified TG-Tv screenings is in use at JSC "Zakarpatye Metal Works" (Ukraine).

The lot of titanium carbide has been produced with composition and quality in accord with the requirements to commercial-grade titanium carbide powder.

Using titanium carbide powders of improved quality, carbide steel of 6X6B3MΦC + 25% TiC grade has been produced by a liquid-phase sintering method. The billet of this carbidic steel contains a minimum number of pores (average porosity of carbidic steel tablets was 2...3%). It is free of defects associated with oxide films.

Main properties of carbidic steel 6X6B3MΦC + 25% TiC are as follows: HRC hardness after sintering – 50; HRC hardness after quenching – 70; HRC hardness after tempering – 68; bending strength σ_{bend} – 1800 N/mm^2; red hardness – 943 K.

CONCLUSIONS

1. The technology of titanium carbide production by SHS-method from – 0.18 and – 0.45 mm TG-Tv screenings subjected to a special treatment to improve their quality and fire- and explosion-safety has been developed and introduced at JSC "Zakarpatye Metal Works" (Ukraine).

The quality of screenings has been improved by the removal of particles smaller than 0.08 mm which have the highest concentration of impurities of various origin from – 0.18 and – 0.45 mm particles.

Fire- and explosion-safety of screenings was improved by a surface treatment with 5-10% solutions of magnesium, sodium and potassium chloride solutions in a ratio of 1 : 4 : 5 or with a spent electrolyte from magnesium production.

The LCLP has increased 2-3 times while the autoignition temperature rose by 20-80 K so that the TG-Tv screening could be pneumatically classified.

2. Main connections between the quality, yield of good carbide and physico-chemical properties of TG-Tv screenings, ratio of – 0.18 + 0.08 and – 0.45 + 0.08 mm fractions in a charge for titanium carbide production have been established.

Best results were achieved when the charge consisted of - 0.18 + 0.08 and – 0.45 + 0.08 mm screenings in a ratio of 1 : 1 due to a weaker impact of charge structure (inner non-uniformity) on the course of SH-synthesis.

3. The lot of titanium carbide has been obtained complying with the requirements to commercial powder product, %(mass): C_{bound}-18.40; C_{free}-0.85; oxygen – 0.38; hydrogen – 0.003; nitrogen – 0.03; titanium – balance.

Using titanium carbide, test samples of carbidic steel of steel 6X6B3MΦC + 25% TiC grade have been produced with good physico-mechanical properties, minimum porosity, free of defects associated with the presence of oxide films.

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