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PRODUCING TIC-AL CERMET BY COMBUSTION SYNTHESIS OF TIC POROUS SKELETON WITH SPONTANEOUS INFILTRATION BY ALUMINUM MELT

Aleksandr Amosov, Evgeny Latukhin, Emil Umerov, Evgeny Amosov, Petr Kichaev

Samara State Technical University

Ceramic-Metal Composites

Ceramic-metal composite materials (cermets) with a ceramic phase content of 15 - 85 vol.% can have a combination of several valuable properties from the following list [1, 2]:

- low weight,
- low coefficient of friction,
- low coefficient of thermal expansion,
- high values of hardness,
- high-temperature strength,
- heat and erosion resistance,
- thermal and electrical conductivity.

[1] J. R. Tinklepaugh and W. B. Crandall, Cermets. New York: Reinhold Publ. Co., 1960.
[2] K. U. Kainer, Metal Matrix Composites: Custom-Made Materials for Automotive and Aerospace Engineering. Weinheim: Verlag GmbH & Co. KGaA, 2006.

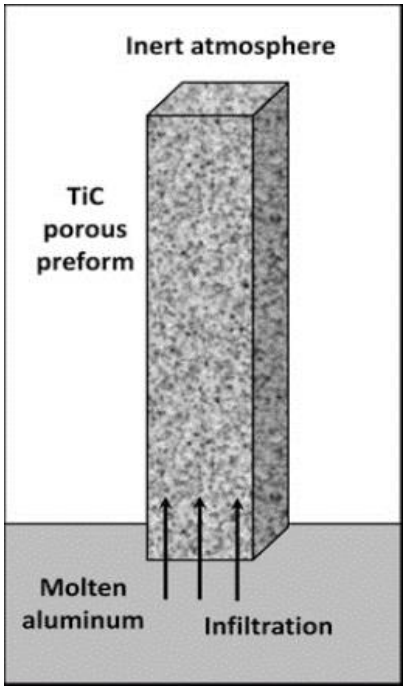
Field of application

Cermets are used as *high-temperature*, *tool* and *special materials* in *metallurgy*, *mechanical engineering*, *aircraft* and *rocket manufacturing*, and *the nuclear power industry*. Also it can been noted their use in *electrical engineering* and *electronics in sliding electrical contacts* and to enhance the emission ability of *cathodes*. Of particular interest are cermets with interpenetrating continuous skeletons of ceramic and metal phases, each of which retains its properties in the macroscopic properties of the composite, providing versatility of these properties, for example, high wear resistance and good electrical conductivity, which is important for sliding electrical contacts [3, 4].

[3] D. R. Clarke, “Interpenetrating Phase Composites,” J. Amer. Ceram. Soc., vol. 75, no. 4, pp. 739-758, 1992.

[4] J. Binner, H. Chang, and R. Higginson, “Processing of ceramic-metal interpenetrating composites,” J. Europ. Ceram. Soc., vol.29, pp. 837 – 842, 2009.

Producing methods of cermets

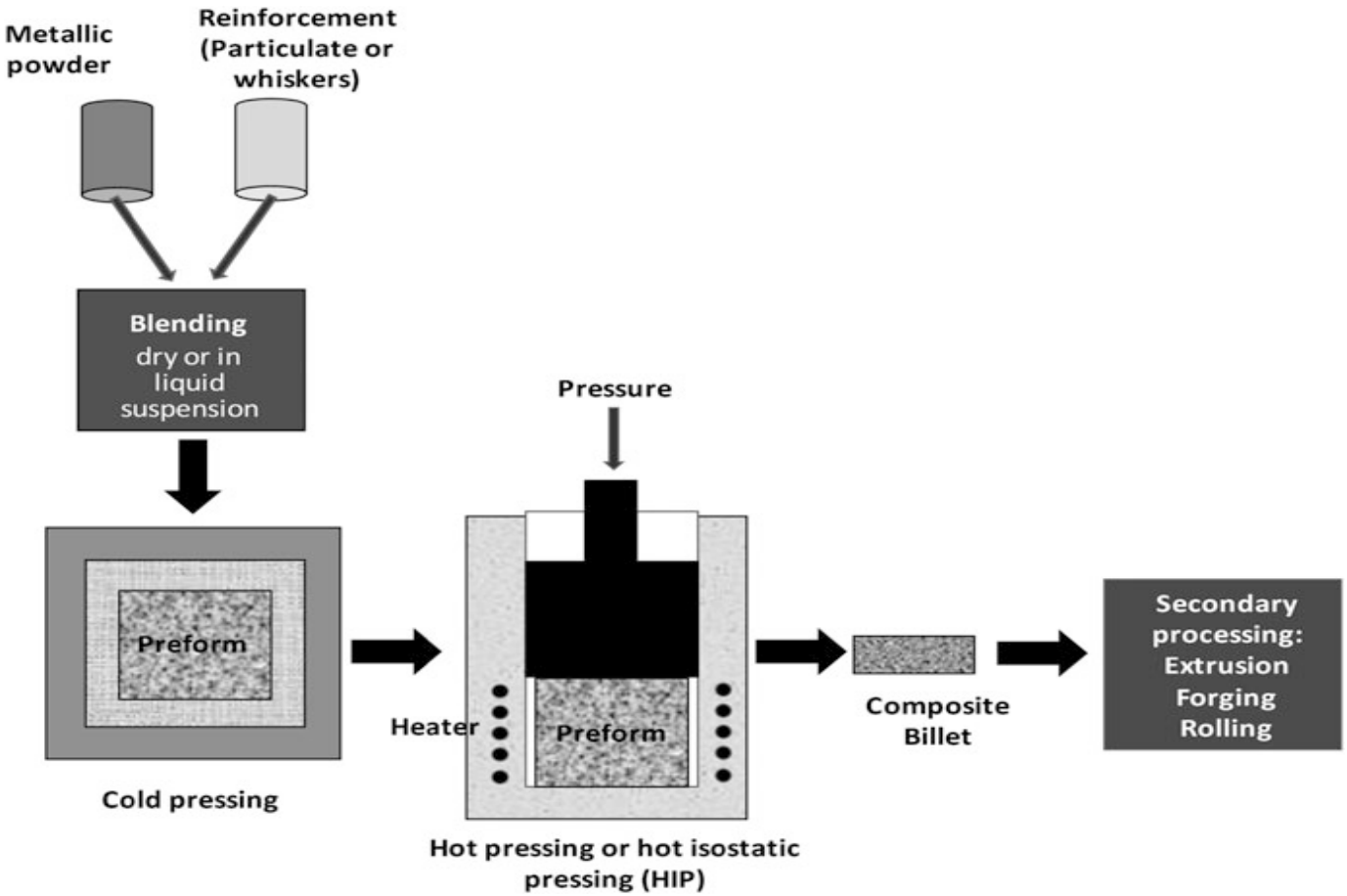


Pressureless infiltration

The most common method is a liquid-state process of the infiltration of a metal melt into a previously prepared ceramic porous skeleton (preform) with filling the pores of the skeleton and solidification on subsequent cooling [4, 5]. Melt infiltration can be **spontaneous** if the metal melt **wets** the ceramic skeleton **well** (pressureless infiltration). If there is no good wettability, then the infiltration is forced, under the influence of external forces: vacuum, applied pressure, vibration, centrifugal or electromagnetic forces.

[4] J. Binner, H. Chang, and R. Higginson, "Processing of ceramic-metal interpenetrating composites," J. Europ. Ceram. Soc., vol.29, pp. 837 – 842, 2009.
[5] A. C. Cuevas, E. B. Becerril, M. S. Martinez, and J. L. Ruiz, Metal Matrix Composites: Wetting and Infiltration. Springer Nature Switzerland AG, 2018.

Producing methods of cermets



A solid-state process of powder metallurgy

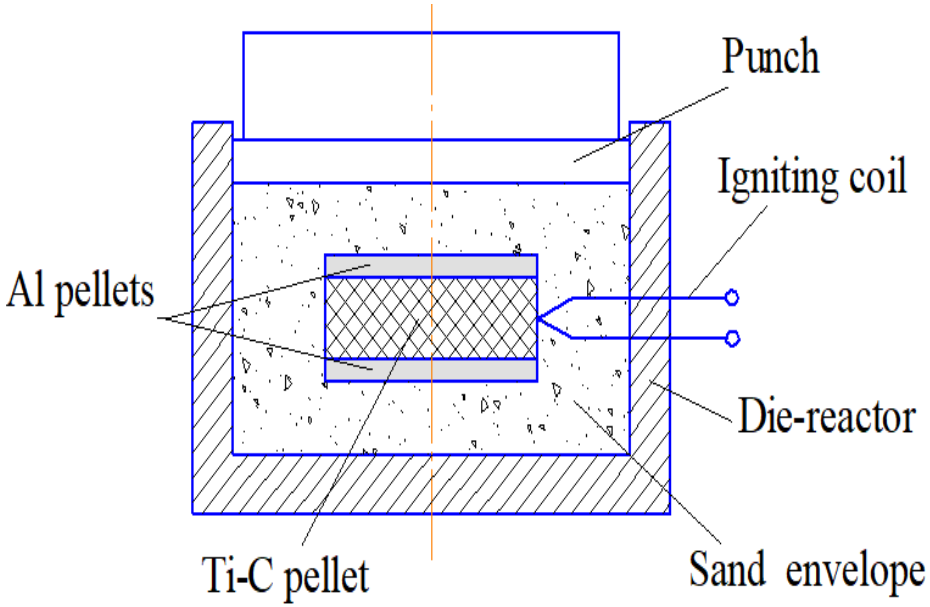
Self-propagating High-temperature Synthesis (SHS)

The use of a more simple and energy-efficient process of SHS of materials or, in other words, the combustion synthesis of materials [6, 7], to prepare ceramic skeletons of increased strength with subsequent infiltration with metal melts can become the basis of a new technology of economically viable production of cermets and contribute to the creation of new materials for modern technics. An important common feature of porous SHS materials is that their strength is usually 1.5-3.0 times higher than that of sintered materials of the same composition with the same porosity [6]. In the case of SHS of titanium carbide by reaction Ti + C = TiC, the final porosity of the synthesized ceramic TiC skeleton averages 50% and is almost completely open porosity [6, 8].

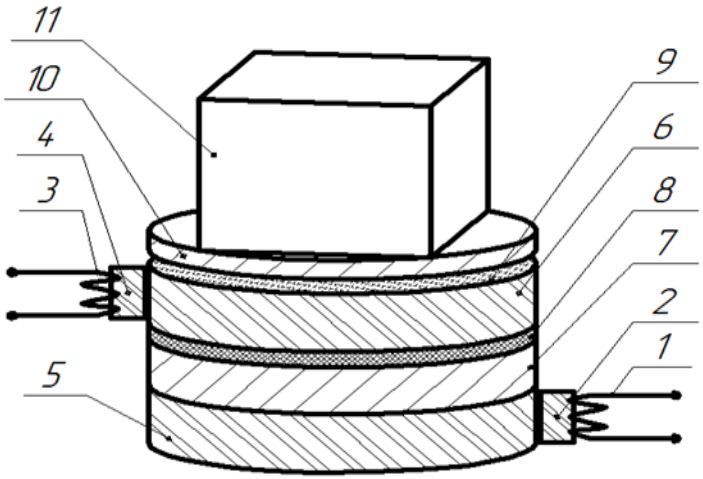
[6] A. P. Amosov, I. P. Borovinskaya, and A. G. Merzhanov, Powder technology of self-propagating high-temperature synthesis of materials. Moskva, 2007. (in Russian).
[7] A. S. Rogachev and A.S. Mukasyan, Combustion for material synthesis. New York, 2014.
[8] A. P. Amosov, A. F. Fedotov, E. I. Latukhin, and V. A. Novikov, "TiC–Al Interpenetrating composites by SHS pressing," Int. J. Self-Prop. High-Temp. Synth., no. 4, pp. 187–191,2015.

Known SHS methods of SamSTU

SHS - Pressing [8]



SHS – Infiltration [9]



Scheme of the experiment on SHS of Ti_3SiC_2 and its infiltration with Cu melt:
1 and 3 – electric heating coils;
2 and 4 - igniting mixtures;
5 and 6 - lower and upper charge briquettes for Ti_3SiC_2 synthesis;
7 - copper powder briquette;
8 - graphite barrier layer; 9 – layer of sand;
10 - metal washer; 11 – load of 500 g.

[8] A.P. Amosov et al. Int. J. SHS, 2015, no. 4. pp. 187-191.
[9] A.P. Amosov et al. J. of Physics. Conf. Ser. 2018, vol. 1115, Art. no. 042003.

A new SHS method to make cermets

Preparation of Ti+C briquettes

Preparation of powders Ti, C

Mixing Ti+C

Weighting

Compaction of charge Ti+C

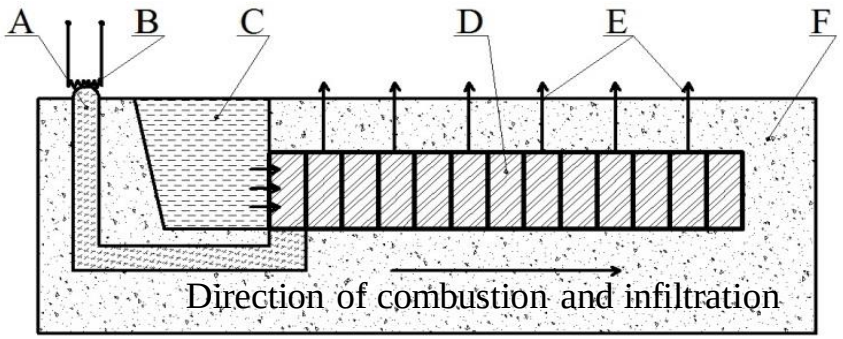
Preparation of Al metal melt

Weighting of solid Al

Preparation of solid Al

Melting of Al

SHS TiC with Al melt infiltration

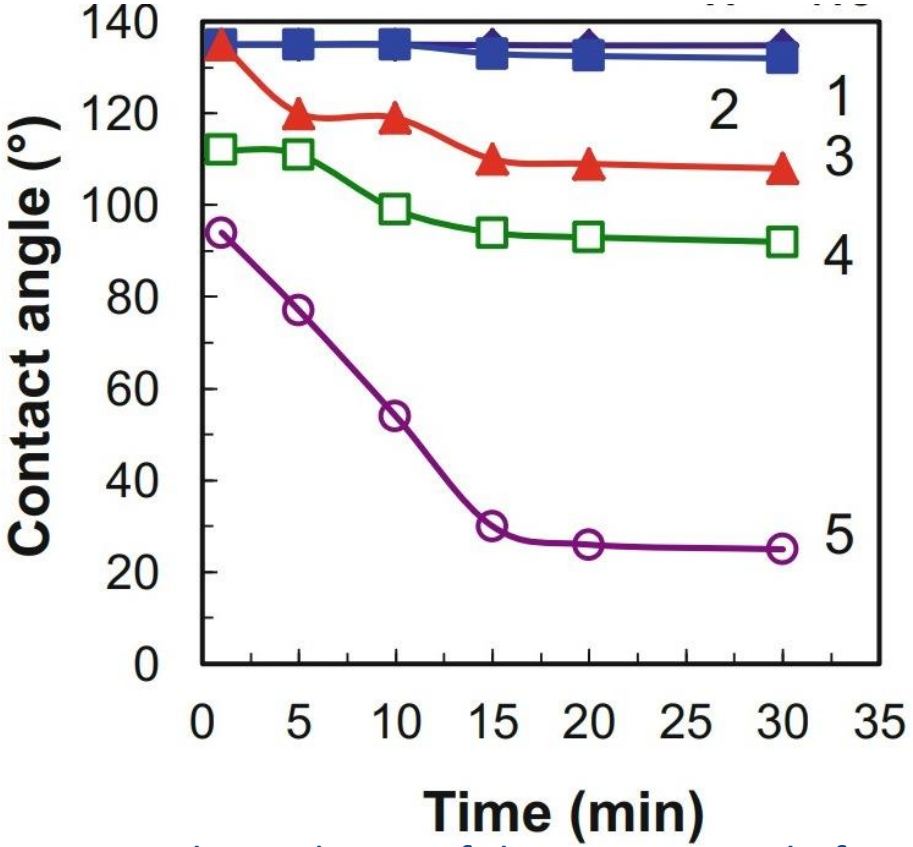


A – Igniting powder mixture, B - Electrical filament, C - Al melt at T = 900°C, D - Charge briquettes of Ti+C powders, E - Gas outlet direction at SHS, F - Sand backfill

[10] A.P. Amosov et al. Appl. For RU Patent Invention 2190682, Nov. 21, 2019.

Theoretical part

Temperature and wetting



Time dependence of the contact angle for TiC with pure Al for (1) 700 °C, (2) 800 °C, (3) 900 °C, (4) 1000 °C, and (5) 1100 °C [5]

For spontaneous infiltration of the porous ceramic TiC skeleton with Al melt, liquid aluminum should wet the ceramic phase well, that is, the contact angle of liquid aluminum on a solid ceramic surface (wetting angle) θ should be less than 90°. The Al/TiC contact angle decreases with increasing temperature and contact time, but the initial value of θ remains greater than 90° even at temperatures of 800-1100°C, and θ decreases below 90° only after 10-30 minutes depending on temperature [5].

[5] A. C. Cuevas, E. B. Becerril, M. S. Martinez, and J. L. Ruiz, Metal Matrix Composites: Wetting and Infiltration. Springer Nature Switzerland AG, 2018.

SHS and wetting

Our experiments showed that immediately after SHS, a hot porous TiC skeleton with a temperature of ~ 2800°C spontaneously absorbs aluminum melt with a much lower temperature (750-900°C). This spontaneous infiltration can be explained by the phenomenon of **thermal osmosis**, that is, the flow of liquid through capillaries under the influence of a temperature gradient at which the thermal osmotic flow is directed in the hot direction in wide lyophilic pores [11]. At very high temperatures of the TiC skeleton ~ 2800°C, the initial value of the angle of wetting with liquid aluminum θ can be significantly less than 90°, which ensures the lyophilic nature of the pores of the ceramic skeleton.

[11] N. V. Churaev, B. V. Derjaguin and V. M. Muller, Surface Forces. Springer; Softcover reprint of the original 1st 1987 edition, 2013.

SHS and wetting

The minimum required temperature to ensure spontaneous impregnation of the TiC skeleton with Al melt is determined by the Ryazanov formula [12]:

$$T_{TiC} = \frac{16450}{13.87 - \lg(S_{SS} - \sigma(T))}$$

where $\mathbf{S_{ss}}$ is the specific surface area of porous TiC, m^2/m^3; **σ(T)** is the surface tension of aluminum, J/m2.

Our estimation shows the temperature of the TiC skeleton must exceed 1730°C to ensure spontaneous infiltration of the skeleton by Al melt.

The depth of penetration of the melt through the capillaries of the porous body is highly dependent on the contact time and is described by the Washburn formula [14]:

$$h_W = \frac{2}{\pi}\left[\left(\frac{r \cdot \sigma \cdot \cos(\theta)}{2\eta}\right) \cdot t\right]^{0.5}$$

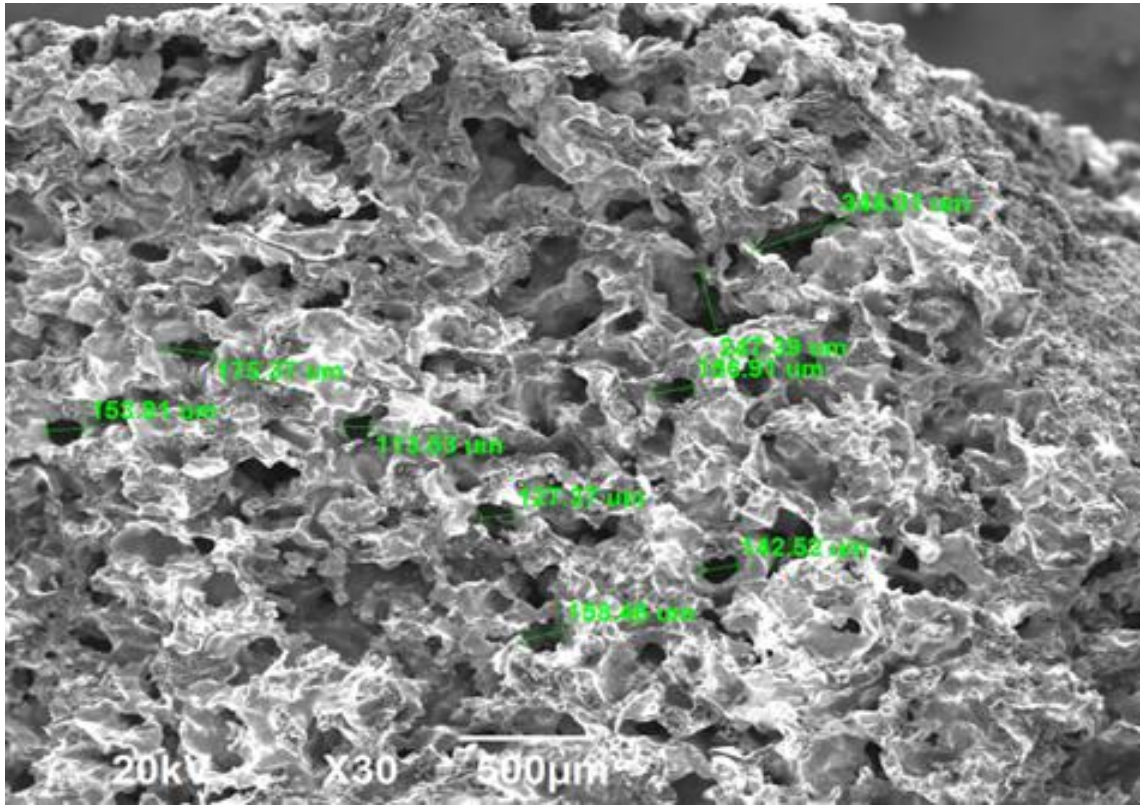
where **r** is the average radius of capillaries, m; **θ** is the wetting angle; **η** is the dynamic viscosity of the melt, Pa•s; **t** is the contact time, s.

Our calculation result of 200 mm is obtained, which can be taken as an upper estimate of the depth of infiltration in the real porous TiC skeleton under consideration.

[12] S. A. Ryazanov, “A method of manufacturing aluminum alloys,” RU Patent 2190682, Oct. 10, 2002. (in Russian).

[14] D. Muscat and A. L. Drew Robin, “Modeling the infiltration kinetics of molten aluminium into porous titanium carbide,” Metallurg. Mater. Trans. A, vol. 25A, pp. 2357-2361, 1994.

Porous structure of TiC skeleton



Average pores radius r = 75 µm was estimated by photomicrographs using SEM «Jeol JSM-6390A» and used in our calculations (Fig. 1).

Experimental part

Due to the technological complexity of preparation of an one-piece compacted charge preform of large length with a uniform distribution of the density of the Ti + C powder mixture, 13 separately compacted cylindrical charge briquettes with a height of 10 mm were made, which were tightly folded together in contact with their bases one by one. The total length of such a charge preform was 130 mm. The **resulting TiC-Al composite sample**, taken out from sand after infiltration with a 900°C melt, is shown in Fig. 3.

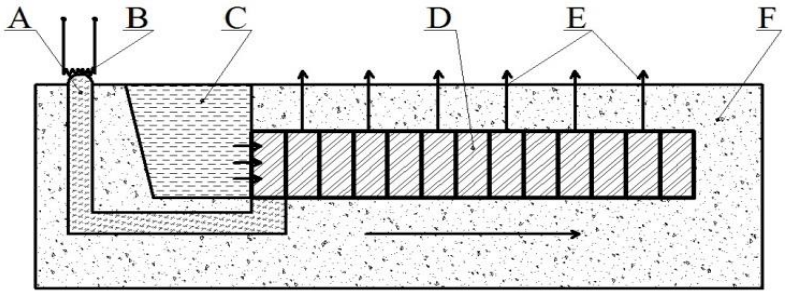


Fig. 2 - Scheme for producing the TiC-Al composite by the SHS method with infiltration. (A – Igniting powder mixture, B - Electrical filament, C - Al melt at T = 900°C, D - Charge briquettes of Ti+C powders, E - Gas outlet direction at SHS, F - Sand backfill).

Fig. 3 - Sample of TiC-Al composite after horizontal unidirectional mode of infiltration with a melt of 900°C.

Density of the TiC-Al composite

The single-piece sample of the TiC-Al composite was mechanically divided into composite briquettes corresponding to the initial charge briquettes to determine the density of each.

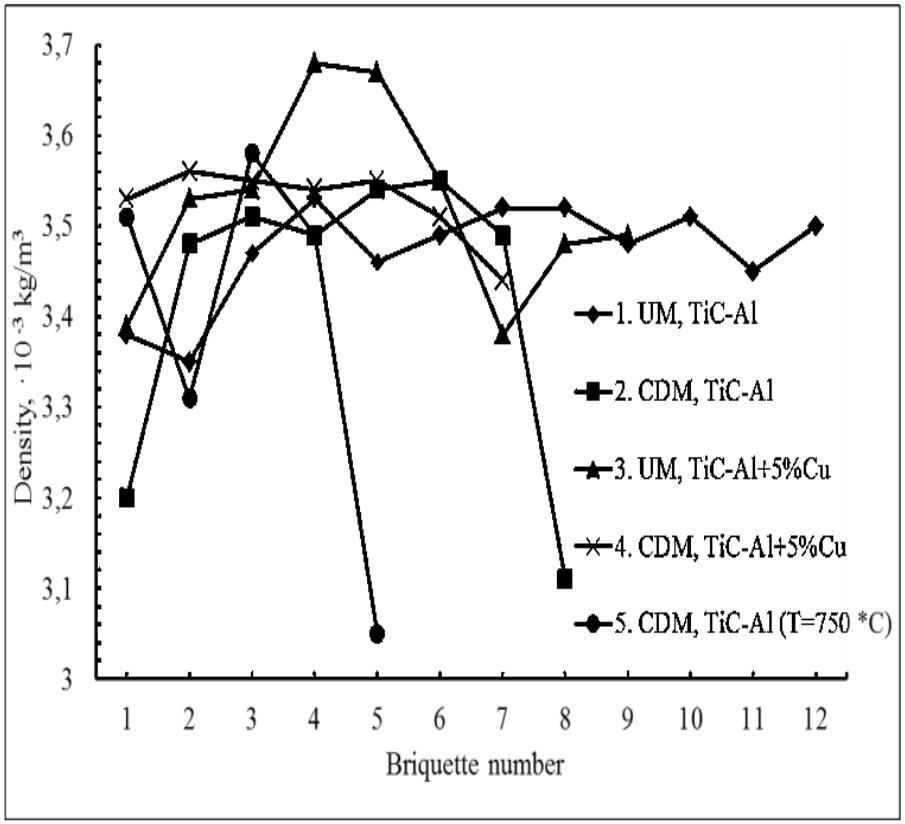


Fig. 4. Diagram of density values of individual briquettes of TiC-Al composite sample for various modes of infiltration with a melt of 900°C and 750°C. (UM – Unidirectional Mode; CDM – Counter Directional Mode).

At unidirectional impregnation with a melt of pure aluminum with a temperature of 900°C, it was possible to impregnate 12 briquettes of TiC. The addition of 5% Cu to the Al melt leads to a decrease in the impregnation length in the unidirectional mode to 9 briquettes. With counter directional infiltration, the impregnation length is even lower and amounts to 8 and 7 briquettes for Al and Al + 5% Cu, respectively.

Al melt with a temperature of 750°C impregnates only 5 briquettes. Edge briquettes are distinguished by less dense due to incomplete impregnation (briquettes no. 7 and no. 8).

In general, the major portion of the briquettes has approximately the same density of about **(3500 ± 150)•kg/m3**, which indicates a fairly complete infiltration (the density 3500 kg/m3 corresponds to the calculated porosity 11.5%) and uniform distribution of Al.

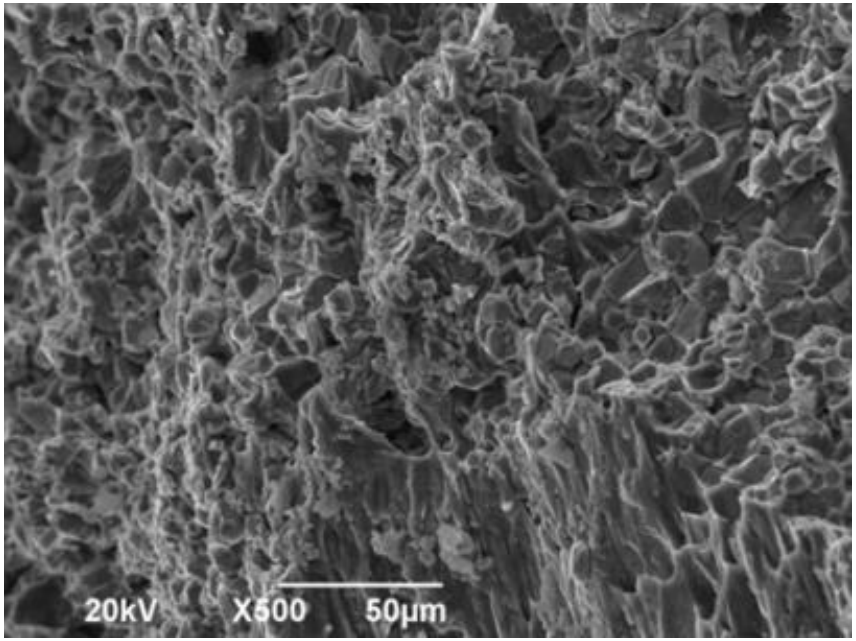
Vertical impregnation

Fig. 5. TiC-Al composite sample after vertical unidirectional mode of infiltration with a melt of 900°C.

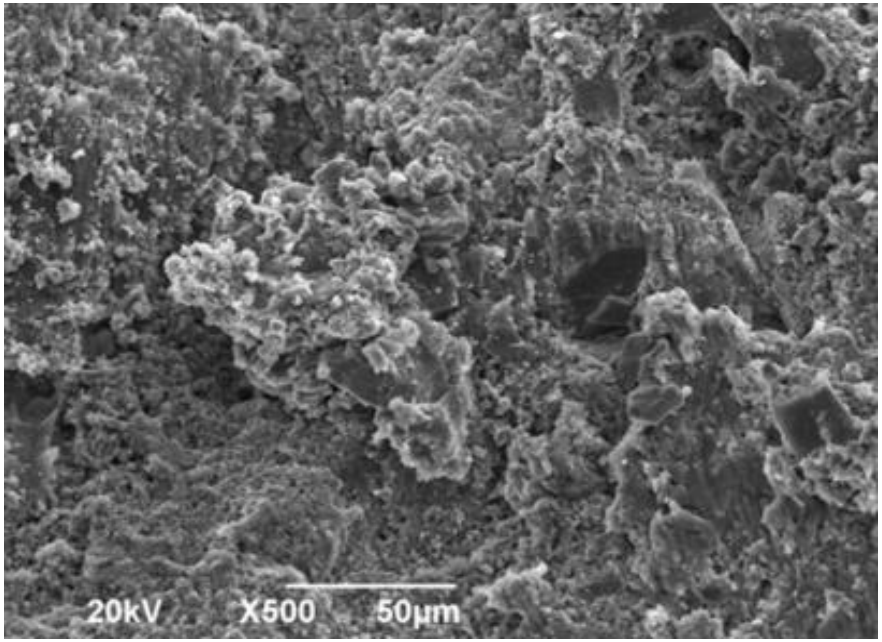
To assess the ability of the Al melt to infiltrate upward through the TiC capillaries, against the action of gravity, we took four briquettes of the Ti + C mixture pressed into cylindrical charge briquettes (D = 23 mm, H = 12 mm), which were mounted on top of each other. The total height of the charge preform was 48 mm. After ignition of the lower briquette contacting with Al melt, a full infiltration to a height of 48 mm was obtained but the lower briquette was upset (Fig. 5).

The infiltrated sample of the TiC-Al composite was not deformed and retained the initial geometric dimensions and shape of the three upper briquettes. **The possibilities of producing large-sized samples of the TiC-Al composite by vertical infiltrtion are limited** by the increasing pressure of the column of the upper part on its lower part.

Microstructure of TiC-Al composite



(a)



(b)

Fig. 6. SEM image of fracture surface of briquettes **no. 2 (a)** and **no. 12 (b)**

The microstructure of briquette **no. 2** has a distinct boundary between TiC grains. Briquette **no. 12** has smaller TiC grains. Briquettes **no. 2** and **no. 12**, which differ in microstructure, also have differences in phase composition established using X-ray diffraction (XRD) analysis.

Phase composition of TiC-Al

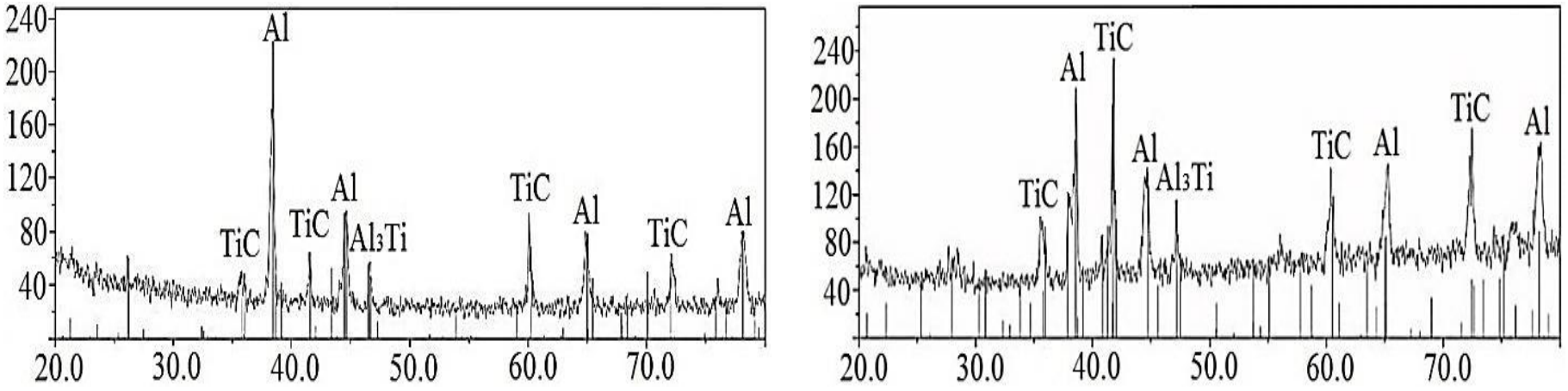


Fig. 7. XRD patterns of briquettes no. 2 (a) and no. 12 (b)

The height of the TiC peaks in the briquette no. 2 is less than in the briquette no. 12, which may indicate the dissolution of TiC by the aluminum flow. The diffraction pattern of briquette no. 12 also shows an increased content of the Al3Ti phase, which is probably brought by aluminum flow to briquette no. 12 from previous briquettes. There is also a bifurcation and/or shift of Al peaks, which may indirectly indicate the presence of carbon in the form of the Al4C3 phase, which is not explicitly detected due to its low content.

Compressive Strength of TiC-Al

With a relative deformation of 11-16%, a sharp increase in deformation is observed, accompanied by the appearance of large cracks in the sample.

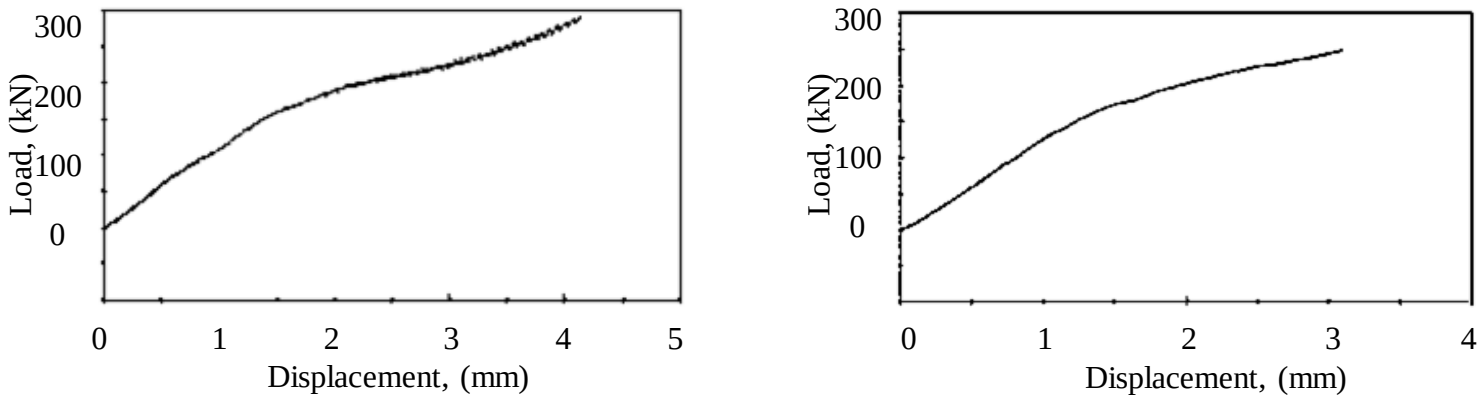


Fig. 8. Loading graphs of TiC-Al composites: (a) CDM, Al + 5% Cu, T = 900°C; (b) UM, Al, T = 750°C

This moment was taken as the tensile strength for cermet samples: **330-390 MPa** (150-180 kN according to Fig. 8). However, a further increase in load showed that the sample continues to deform, while retaining the **bearing capacity up to 500-650 MPa** (250-290 kN). This indicates a significant strength of the obtained TiC-Al cermet samples, if we take into account that the compressive strength of pure aluminum A7 brand is 75 MPa.

CONCLUSION

Thus, it was confirmed that a new method for applying the SHS process for the synthesis of a ceramic porous TiC skeleton followed by spontaneous infiltration with previously prepared aluminum melt allows producing TiC-Al cermets with a volumetric content of titanium carbide of ~ 50% without applying external pressure.

- Theoretical estimates have been received of both the temperature of the synthesized porous TiC skeleton (≥1730°C), necessary for spontaneous infiltration by Al melt via the phenomenon of thermal osmosis, and the depth of spontaneous infiltration (up to 200 mm).
- It has been experimentally shown that spontaneous infiltration in various conditions (horizontal or vertical, unidirectional or counter direction modes) can have a depth of 48 mm to 130 mm.
- Generally, the bulk of the cermet samples obtained have approximately the same density of about 3500 kg/m3, which corresponds to a porosity of 11.5% and indicates a rather complete infiltration and uniform distribution of Al.
- Along with the main TiC and Al phases, cermet samples may contain impurities of the Al3Ti and Al4C3 phases.
- The compressive strength of samples of TiC-Al composites reaches 330-390 MPa, when the first signs of fracture of the samples in the form of cracks appear, however, complete destruction does not occur, and the bearing capacity is maintained even at 500-650 MPa.

Acknowledgment

The reported study was funded by RFBR, project number 20-08-00435.

Thank you for attention!