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Investigation of possibility of fabrication of long-length samples of Ti_3AlC_2–Al MAX-cermet by the SHS method with spontaneous infiltration by aluminum melt

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Abstract: The article discusses the features of combining the self-propagating high-temperature synthesis (SHS) of the Ti_3AlC_2 MAX phase porous skeleton with infiltration by aluminum melt in a spontaneous mode in order to obtain enlarged samples of Ti_3AlC_2–Al ceramic-metal composite (MAX cermet) in an air atmosphere. A new scheme was developed for obtaining long-length SHS cermet samples from a bulk density charge with spontaneous infiltration by melt in the same direction with the combustion wave movement, which makes it possible to regulate the time gap between the end of the Ti_3AlC_2 synthesis and the beginning of the spontaneous pore filling with aluminum melt. This technology was used to obtain a Ti_3AlC_2 SHS skeleton with a total length of 250 mm and a diameter of 22–24 mm where the depth of infiltration with pure aluminum was about 110 mm, and impregnation with the Al–12%Si alloy was 130 mm. The paper provides comparative data on density, microstructure, and phase composition at different areas along the length of MAX cermet samples obtained. It was found that infiltration with pure aluminum destroys the Ti_3AlC_2 MAX phase to transform it into a mixture of TiC + $TiAl_3$ phases in the SHS cermet, and 12 % Si added to the Al melt promote Ti_3AlC_2 preservation in the cermet to a some extent. Instead of MAX cermet samples with the target composition of Ti_3AlC_2–Al and Ti_3AlC_2–(Al–12%Si), long-length samples of SHS cermets with a different actual phase composition were obtained: TiC–$TiAl_3$–Al and TiC–Ti_3AlC_2–$TiAl_3$–(Al–12%Si), respectively, where the Ti_3AlC_2 MAX phase either practically absent or present in small quantities. The average hardness values of TiC–$TiAl_3$–Al and TiC–Ti_3AlC_2–$TiAl_3$–(Al–12%Si) SHS cermets were *HB* = 640 and 740 MPa, density ρ = 2.88÷3.16 g/cm^3 and 3.03÷3.13 g/cm^3, and residual porosity *П* = 17.0÷24.6 % and 17.6÷20.3 %, respectively.

Keywords: self-propagating high-temperature synthesis (SHS), MAX phase, Ti_3AlC_2, spontaneous infiltration, MAX cermet, Ti_3AlC_2–Al, microstructure, phase composition, physical and mechanical properties.

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Исследование возможности получения длинномерных образцов MAX-кермета Ti_3AlC_2–Al методом СВС с самопроизвольной инфильтрацией расплавом алюминия

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Аннотация: Рассмотрены особенности совмещения процесса самораспространяющегося высокотемпературного синтеза (СВС) пористого каркаса MAX-фазы Ti_3AlC_2 с инфильтрацией расплавом алюминия в самопроизвольном режиме с целью

получения образцов керамико-металлического композита (MAX-кермета) Ti_3AlC_2–Al увеличенных размеров в воздушной атмосфере. Разработана новая схема изготовления длинномерных образцов СВС-керметов из шихты насыпной плотности с самопроизвольной инфильтрацией расплавом в спутном направлении с движением волны горения, при которой можно регулировать временну́ю паузу между моментом окончания синтеза Ti_3AlC_2 и началом процесса самопроизвольного заполнения пор расплавом алюминия. По данной технологии был синтезирован СВС-каркас Ti_3AlC_2 общей длиной 250 мм и диаметром 22–24 мм, в котором глубина инфильтрации чистым алюминием составила около 110 мм, а пропитка сплавом Al–12%Si – 130 мм. Приведены сравнительные данные по плотности, микроструктуре и фазовому составу на разных участках по длине образцов полученных СВС-керметов. Установлено, что инфильтрация чистым алюминием разрушает MAX-фазу Ti_3AlC_2, превращая ее в смесь фаз TiC + $TiAl_3$ в СВС-кермете, а добавка 12 % Si к Al-расплаву способствует некоторому сохранению Ti_3AlC_2 в кермете. Вместо образцов MAX-керметов с целевым составом Ti_3AlC_2–Al и Ti_3AlC_2–(Al–12%Si) получены длинномерные образцы СВС-керметов с другим реальным фазовым составом: TiC–$TiAl_3$–Al и TiC–Ti_3AlC_2–$TiAl_3$–(Al–12%Si) соответственно, в которых MAX-фаза Ti_3AlC_2 или практически отсутствует, или имеется в небольших количествах. Средние значения твердости СВС-керметов TiC–$TiAl_3$–Al и TiC–Ti_3AlC_2–$TiAl_3$–(Al–12%Si) составили *HB* = 640 и 740 МПа, плотность ρ = 2,88÷3,16 и 3,03÷3,13 г/см^3, а остаточная пористость *П* = 17,0÷24,6 и 17,6÷20,3 % соответственно.

Ключевые слова: самораспространяющийся высокотемпературный синтез (СВС), MAX-фаза, Ti_3AlC_2, самопроизвольная инфильтрация, MAX-кермет, Ti_3AlC_2–Al, микроструктура, фазовый состав, физико-механические свойства.

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Introduction

In the past 25 years MAX phases including titanium aluminum carbide (Ti_3AlC_2) have been attracting much attention. Their unique properties combine the advantages of ceramic and metallic materials as demonstrated in [1, 2]. So far more than 150 different MAX phases have been synthesized and studied. MAX phases have not yet been applied commercially [2], however, despite their large number and attractive properties arising from their unique layered crystal structure, low weight, excellent oxidation resistance up to 1400 °C in aggressive environment, high resistance to mechanical damage, thermal shock and radiation, crack bridging, and good machinability by both cutting and electrical erosion. One notable exception is chromium aluminum carbide (Cr_2AlC), which is used in sliding current collectors instead of carbon current collectors on high-speed trains in China.

The main limiting factor in transferring MAX phases to the market is the absence of suitable methods for producing high-purity MAX phases in large quantities at an acceptable cost [2]. In this respect, one of the most promising methods could be self-propagating high-temperature synthesis (SHS). This is characterized by simplicity, short synthesis time, low energy consumption, flexibility and possibility of increasing the production scale, as well as an acceptable cost of synthesis products [2—4]. The main drawback of this technology is the high content of side phases and impurities (carbides, intermetallic compounds, and residues of unreacted reagents) in the synthesized MAX phases. With this in mind, the further development and improvement of the SHS method as a process foundation for the creation of economically justified facilities, i.e. the commercialization of MAX phases and new ceramic and composite materials and products based on them is of undoubted interest.

This work considers the application of the SHS method for the synthesis of the porous framework of the Ti_3AlC_2 MAX phase followed by spontaneous infiltration with aluminum melt to obtain a ceramic-metal composite (MAX cermet) Ti_3AlC_2—Al of increased

dimensions in air atmosphere. (MAX phase composites with metals are referred to as «MAXMETs» or «MAX-MMCs» in English-language literature [5—7], but in Russian-language sources we propose the name «MAX cermet», given that MAX phases refer to new ceramics [8, 9]). Compound Ti_3AlC_2 is one of the most popular MAX phases and is characterized by low weight, good crack resistance, ductility and oxidation resistance at high temperatures. This makes its use very attractive in composite materials with metals, i.e. in MAX cermets, in aerospace engineering [6, 9, 10]. Metal Al-bonded Ti_2AlC and Ti_3AlC_2 titanium aluminum carbide-based cermets have high values of the yield strength, impact strength and mechanical energy dissipation [11, 12]. They are considered much more effective than aluminum and other metals for the protection of spacecraft against high velocity impacts from micrometeorites and orbital debris.

Both solid-phase powder metallurgy and liquid-phase infiltration methods can be used to manufacture framework MAX cermets [13]. For example, Ti_3AlC_2—Al cermets were fabricated from pure Al powders and 40 vol.% Ti_3AlC_2 by hot isostatic pressing [12]. It was found that nanocrystalline agglomerates of Ti_3AlC_2, distributed evenly in the Al matrix, form a solid continuous framework. Evaluation of the mechanical properties of cermets in the temperature range of 20—500 °C by conducting compression tests at a constant deformation rate showed that the yield strength of cermet was about 2 times higher than that of aluminum matrix in the temperature range under study. New cermet Ti_3AlC_2—Al_3Ti—Al was fabricated by hot pressing of Ti_3AlC_2 and pure Al powders [14]. Strong interfacial bonding occurred due to the formation of the Al_3Ti phase between Ti_3AlC_2 and Al. The bending strength, compressive strength, compressive yield strength and Vickers hardness number of cermet reinforced with 30 vol.% Ti_3AlC_2 were measured. These were 398 MPa, 404 MPa, 359 MPa, and 1.91 GPa, respectively.

Methods of infiltration (impregnation) of a porous ceramic framework with metal melt are one of the most common technologies used in the production of cermets. They allow products of complex shape with low residual porosity and low cost to be obtained, when compared to the methods of powder metallurgy. This is due to the possibility of using relatively inexpensive foundry equipment [13].

Methods using spontaneous infiltration without the application of external pressure are the simplest and therefore most attractive. However, the spontaneous impregnation of a ceramic framework is possible only when the metal melt wets the ceramics, i.e., when the contact angle is $\theta < 90°$. The smaller the value of θ, the easier infiltration takes place.

The wetting angle depends on the nature of the ceramic and metal phases, the temperature and duration of their contact, and the gas environment. MAX phases of titanium Ti_3SiC_2, Ti_3AlC_2 and Ti_2AlC, similar to titanium carbide (TiC), are not wetted by pure liquid aluminum ($\theta > 90°$) at temperatures below 900 °C. This is due to the presence of an oxide film and contamination on the MAX phase surface. However, at higher temperatures and over time, the contact angle decreases to values of $\theta < 90°$, i.e., wetting begins. This is explained by the fact that wetting is determined by chemical reactions at the interface and their influence on the destruction of the oxide film on the surface.

As noted in [15], little information is available at the present time on the use of the infiltration method to produce MAX cermets with an aluminum metal phase. The same work demonstrates that MAX cermet systems of the titanium—aluminum aluminum carbide system, namely Ti_3AlC_2—2024Al with a framework structure, can be produced successfully from porous Ti_3AlC_2 blanks by infiltration without pressure by aluminum alloy melt 2024Al at t = 930 °C [15]. Ti_3AlC_2 blanks with porosity of 48, 41 and 35 % were previously obtained by vacuum sintering at t = 1450 °C from Ti, Al and TiC powders. During infiltration lasting 180 min, the reaction between Ti atoms deintercalated from porous Ti_3AlC_2 and Al atoms from liquid 2024Al in pores formed intermetallic compound Al_3Ti to the amount of 15 to 28 vol.% with a Ti_3AlC_2 framework porosity from 35 to 48 % respectively. At room temperature, cermet formed from the Ti_3AlC_2 framework with a porosity of 41 %, composition, vol.% of $52Ti_3AlC_2$—$19Al_3Ti$—29Al, and relative density of 95.41 %, showed the best set of mechanical properties: flexural strength of 510 MPa, compressive strength of 729 MPa and compressive strain of 5.49 %.

The authors of [10] obtained porous frameworks of the MAX phase of Ti_3AlC_2 by SHS after heating in a microwave oven. Then after cooling they were transferred to a metal mold, heated to 750 °C and impreg-

nated for 1—2 minutes with aluminum cast alloy melt Al—13%S at 720—740 °C by casting under the pressure of 90 MPa. The quantitative *X*-ray Diffraction (XRD) phase analysis showed that SHS produced a ceramic framework of two major phases Ti_2AlC and Ti_3AlC_2, as well as a small amount of TiC, wt.%: Ti_2AlC — 66.54, Ti_3AlC_2 — 30.32, and TiC — 3.14. After infiltration under pressure by the Al—13%Si melt, the MAX cermet was formed with a volume ratio of the ceramic and metal phases of about 50 : 50 and a relative density of at least 95 %. Due to the short duration and low temperature of the infiltration process side intermetallic phase Al_3Ti is not formed. The hardness of the cermet increased by a factor of 4 relative to the soft matrix (Al—13%Si), 588 HV versus 160 HV, and the wear rate was less than half that of the Al—13%Si alloy.

In the above examples using infiltration, the MAX cermets of the Ti_3AlC_2—Al system were produced using 2-stage technologies with long external heating at high temperatures, i.e., at sophisticated equipment and with high energy consumption. Single-stage energy-saving process of force SHS compaction allows the thermal effect of SHS to be used for both the synthesis of the Ti_3AlC_2 MAX phase framework and simultaneous melting of aluminum, and its rapid forced infiltration under the pressing pressure into the synthesized framework in obtaining a compact Ti_2AlC—Al MAX cermet [16].

However, the simplification of this approach by refusing to use sophisticated pressing equipment, while using the SHS process both for the synthesis of the MAX phase framework and for the simultaneous melting of the metal and its spontaneous infiltration into the framework without applying excessive pressure results in a non-uniform composition of MAX cermet with partially filled pores in the framework [17]. This can be explained by the fact that only a small amount of metal can be melted due to the SHS reaction heat. This is insufficient for complete filling of pores in the MAX phase framework by spontaneous infiltration. The SHS heat consumption for heating and melting of aluminum leads to rapid cooling of the SHS framework, making it difficult to wet it with a metal melt and complicating the flow of spontaneous infiltration.

In this regard, the authors of this paper propose a new simple method of obtaining cermets based on the use of the porous ceramic framework SHS process, followed by spontaneous infiltration with a metal melt prepared in advance by heating from an external source. This allows the requisite amount to be used, in order to completely impregnate the ceramic framework of sufficiently large dimensions without applying excess pressure. This was successfully demonstrated by the example of obtaining the TiC—Al cermet [13, 17]. This technology was used to produce MAX cermets Ti_2AlC—Al and Ti_3AlC_2—Al in the form of small samples. They were obtained by air burning of briquettes pressed at 25 MPa (23 mm in diameter and 10 mm high) of the corresponding mixtures of titanium, aluminum and graphite powders with an average delay time of 8 s after completion of burning, and the subsequent immersion of the synthesized hot MAX phase framework into the aluminum melt or its pouring with Al melt for spontaneous infiltration of the SHS framework [18, 19].

The study of the possibility to produce samples of MAX cermets of increased sizes compared to those obtained earlier by the new method is of undoubted interest. This would include long samples whose length is several times greater than the diameter of their cross-section. Long samples of the TiC—Al cermet in the form of cylindrical rods up to 130 mm long were obtained from a composite charge blank of 13 separately pressed charge briquettes (10 mm high and 23 mm in diameter), tightly pressed to each other with ends touching. It is technologically difficult to produce a one-piece pressed charge blank of a significant length with uniform charge density distribution [13].

The purpose of this work was to investigate the possibility of applying a new simpler flowchart to use of the SHS process with spontaneous infiltration with aluminum melt, in order to obtain long Ti_3AlC_2—Al MAX cermet samples from a bulk density charge in air atmosphere, taking into account the features of formation of the Ti_3AlC_2 MAX phase.

Research materials and methods

Previous studies have shown that the structure and fractional composition of initial powder reagents significantly affect the Ti_3AlC_2 content in the SHS framework, as well as its structure after synthesis in air atmosphere [20]. Therefore, in the present work, the grades of titanium TPP-7 (d ~ 300 μm, purity 97.9 %), alumi-

num PA-4 (~50 μm, 99 %) and graphite S-2 (~15 μm, 98.5 %) were selected as the main powder reagents which allow the SHS framework to by synthesized in the air with the highest Ti_3AlC_2 content without significant macrostructural defects, cracks, large pores, etc. Aluminum melt with a temperature of 900 °C for the SHS framework infiltration was prepared from A85 grade aluminum (purity not less than 99.7 %) in a Graficarbo electric furnace (Italy). The Al—12%Si alloy was obtained by dissolving silicon in aluminum melt.

Pre-dried initial powders were mixed in a ball mill for 20 min. The powder charge mixture of 3Ti + Al + + 2C was poured into a cylindrical single-layer paper cup 22 mm in diameter and 250 mm long without additional compaction. The SHS reaction was carried out by burning the charge in bulk inside a paper cup placed horizontally on a sand base. The burning of the charge was initiated with a nichrome electric glow spiral by means of ignition charge of TPP-7 grade titanium and P701 carbon black powders with a mass ratio of 4 : 1.

The ignition charge supplied a thermal impulse to the charge at a distance of 40 mm from the place of contact of the charge blank with the Al melt bath. Initiation of the ignition charge and pouring of the melt into a recess prepared in the sand were carried out simultaneously. SHS reaction startup from the contact of the charge with the hot melt did not occur. Taking into account the experimentally determined velocity of the burning wave (~6 mm/s), this distance (40 mm) enabled a pause of 5—6 s, sufficient for completion of secondary structure formation in the burned SHS framework and synthesis of Ti_3AlC_2.

The burning velocity was determined by video filming (at a frequency of 60 frames per second) of the burning process of a 200 mm long charge blank. The video image was analyzed to determine the length of the burned SHS framework to the time of its burnout ratio. The experiment flowchart is shown in Figure 1. Its data shows that the SHS initiation site can be shifted along the charge blank by adjusting the pause between the passage of the burning wave and the infiltration front. The ability to adjust the pause is necessary to provide a certain time delay for charge mixtures of different compositions and press densities, which can have significantly different burning rates.

The SHS cermet obtained was divided into equal cylinders 20 mm long, in order to study the microstruc-

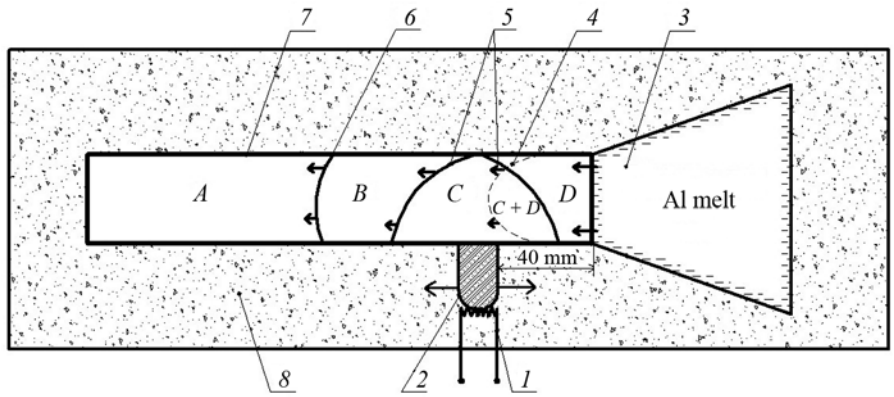

Fig. 1. Ti_3AlC_2–Al SHS cermet production diagram (top view)

1 – filament, ***2*** – igniter, ***3*** – Al melt at t = 900 °C, ***4*** – melt infiltration front, ***5*** – conditional front of Ti_3AlC_2 secondary structure formation, ***6*** – burning front, ***7*** – SHS charge, ***8*** – sand

A – area of 3Ti–1Al–2C initial reagents; ***B*** – area of TiC_x + $TiAl_x$ primary structure formation; ***C*** – area of Ti_3AlC_2 secondary structure formation; ***D*** – area of Al infiltration; (***C*** + ***D***) – Ti_3AlC_2 area containing infiltrated aluminum in pores

Рис. 1. Схема получения СВС-кермета Ti_3AlC_2–Al (вид сверху)

1 – спираль накаливания, ***2*** – запал, ***3*** – Al-расплав с t = 900 °C, ***4*** – фронт инфильтрации расплавом,

5 – условный фронт вторичного структурообразования Ti_3AlC_2, ***6*** – фронт горения, ***7*** – шихта СВС, ***8*** – песок

A – область исходных реагентов 3Ti–1Al–2C; ***B*** – область первичного структурообразования TiC_x + $TiAl_x$;

C – область вторичного структурообразования Ti_3AlC_2; ***D*** – область инфильтрации Al;

(***C*** + ***D***) – область Ti_3AlC_2, содержащая инфильтрированный алюминий в порах

ture and phase composition at a certain distance from the beginning of the sample contacting the molten metal. The microstructure of the samples was studied using a scanning electron microscope (SEM) JSM-6390A (JEOL Ltd., Japan). Phase composition was determined by means of *X*-ray diffractometer ARL X'trA-138 (Thermo Scientific, Switzerland) using CuK_α radiation with continuous scanning in the interval of angles $2\theta = 5°\div80°$ with the speed of 2 deg/min. Sample density was evaluated by hydrostatic weighing in water. Hardness (*HB*) was measured using the Brinell method by indentation of a steel ball (d = 5 mm) with a load of 2,5 kN, since a relatively large ball allows averaging of structural heterogeneities (small pores).

Results and discussion

Preliminary experiments on the use of SHS to produce MAX cermets by initiating burning at the place of contact of the charge with the melt showed the impossibility of preserving the MAX phase in the final composite. The introduction of the cooler metal melt into the hot SHS framework resulted in its rapid cooling and inhibiting high-temperature reactions of formation of titanium aluminum carbide MAX phases. This occurred in the afterburning zone for at least 4—6 s after the burning wave passed [21]. Therefore, conditions for the formation of the MAX phase in the afterburning zone can be ensured by adjusting the time pause between the passage of the burning front and the infiltration front. On the other hand, too long a pause can lead to significant cooling of the framework. This can ultimately make it impossible for it to be wetted and spontaneously infiltrated by the aluminum melt or substantially limits the infiltration depth.

When SHS is initiated at a distance of 40 mm from the melt bath, 2 burning fronts are created simultaneously, moving in opposite directions of the charge blank. The first burning front moves towards the melt bath, and after traveling a distance of 40 mm, reaches the beginning of the charge blank at the point of contact with the melt. The already red-hot SHS framework melted the oxide film on the surface of the melt bath. At a burning wave velocity of 6 mm/sm it took about 6—7 s to overcome this distance (40 mm). At this point, the aluminum melt began to infiltrate into the SHS framework, in which the second burning front continued to move in the opposite direction from the melt bath. Thus, a time pause (6—8 s) between the second (main) burning front and the infiltration front was provided.

The appearance of the SHS cermet obtained based on Ti_3AlC_2 is shown in Figure 2. It can be seen that a part of the burnt fuse remained in the upper part of the sample on the left, which at a distance of ~40 mm from the beginning of the sample initiated the SHS reaction, triggering 2 burning waves in different directions. Zone *1* with a length of about 40 mm on the sample was formed first and performed a process function in this circuit. Given that the pause between the end of burning in this zone *1* and the beginning of infiltration was less than 6 s, the function of this section of the SHS framework was reduced, in order to provide a pause between the second burning wave (moving to the right side of the sample) and the infiltration front. The first section of the 100 mm long sample has a larger diameter of 24 mm. It is silver in color, and has a slightly deformed surface, indicating the presence of aluminum in the framework pores. An increase in diameter of the impregnated part of the framework may be due to the Rehbinder effect, as well as features of the high-temperature chemical interaction of the Al melt/silumin with the 3Ti—Al—2C SHS system. The right section measuring 60—70 mm is distinguished by a white plaque and a smaller diameter (~20 mm).

In order to study the completeness and depth of the aluminum melt infiltration into the SHS framework, the MAX cermet samples obtained were cut into 10 approximately equal cylindrical disks with an average thickness of ~14 mm for the Ti_3AlC_2—Al sample with target composition, with an initial length of 160 mm and ~15 mm for the Ti_3AlC_2—(Al—12Si) sample with l = 170 mm. The loss of 20 mm of the total length was due to material consumption when cutting sample disks with a cutting wheel about 2 mm thick. Thus, 9 cross-sections were obtained in succession along the length of MAX cermet samples. The appearance allows the quality of impregnation to be assessed visually.

Figure 3, *a* shows that the first 4 cross-sections practically have no pores or voids, while possessing a homogeneous metallic luster, indicating good wetting of ceramics by metal in this section up to ~60 mm long. In cross-sections *5*—*8*, an increasing number of dark pores can be noted: from few single pores in cross-section *5*;

to the predominance of dark pores over silver pores in cross-section *8*. The images of cross-sections *8* and *9* are characteristic of an unimpregnated SHS framework of Ti_3AlC_2, so conventionally the distance at which cross-section *7* with obvious signs of impregnation was obtained can be taken as the depth of impregnation, i.e., about 110±10 mm.

Figure 3, *b* shows that starting from the first section, small pores are observed from one to several pieces, clearly distinguishable on the homogeneous silver surface of the cut. Cross-sections *4—7* show pore clusters in specific areas of the cross-section. Cross-sections *8* and *9* have the appearance of an unimpregnated framework, with no obvious traces of the presence of significant amounts of metal. Taking into account the average length of each individual sample disk (15 mm) and loss per cut (2 mm), impregnation in this case was completed on the 8th sample disk, and its depth was about 130±10 mm. Increase of the infiltration depth up to ~130 mm may be explained by increased fluidity of the melt and its wetting of the framework in the presence of silicon in the melt.

Figure 4 shows that the density distribution curves of SHS cermets of Ti_3AlC_2—Al and Ti_3AlC_2—(Al—12Si) target compositions have a similar nature and they decrease smoothly along the length of the samples from 3.0—3.2 to 2.0 g/cm^3. At the same time, the density of Al—12Si-based cermet is slightly higher. This may indicate a more complete impregnation with silumin melt, when compared to pure aluminum.

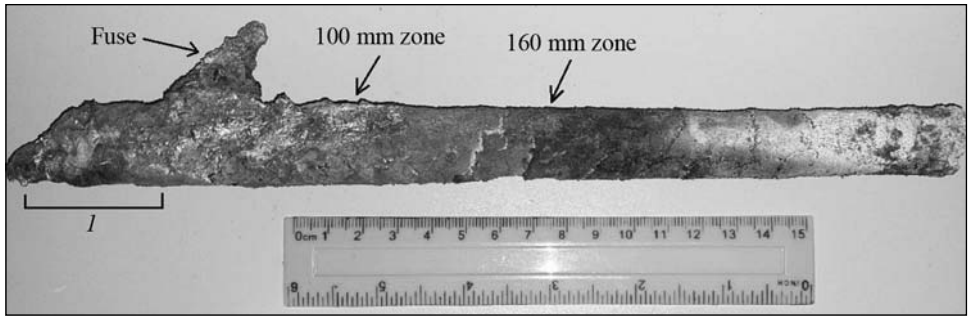

Fig. 2. Cermet sample after SHS

1 – zone from 0 to 40 mm, in which the pause between the SHS process and melt infiltration was less than 6 s

Рис. 2. Образец кермета после СВС

1 – зона от 0 до 40 мм, в которой пауза между процессом СВС и инфильтрацией расплава была менее 6 с

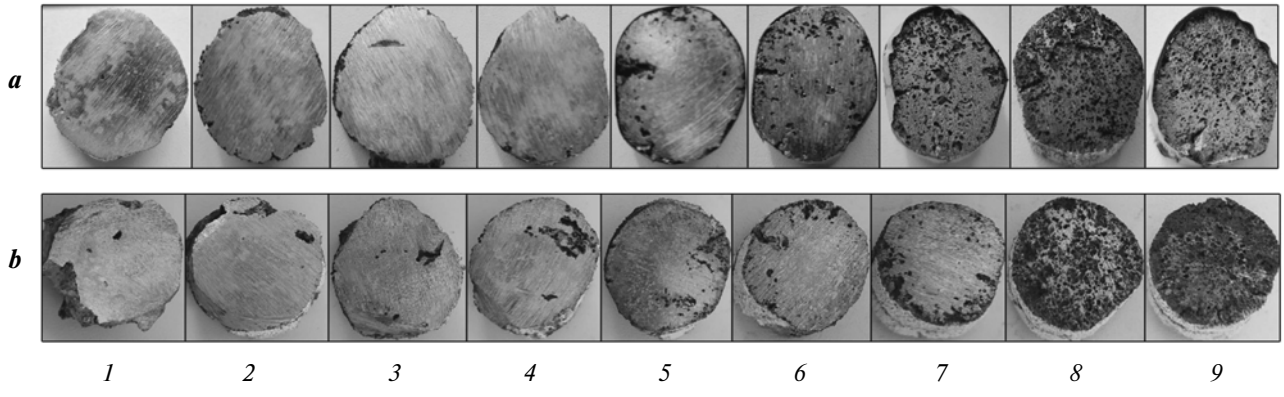

Fig. 3. Successive cross sections of long-length SHS cermets with target compositions Ti_3AlC_2–Al (***a***) and Ti_3AlC_2–(Al–12Si) (***b***)

Рис. 3. Последовательные поперечные сечения длинномерных СВС-керметов целевых составов Ti_3AlC_2–Al (***a***) и Ti_3AlC_2–(Al–12Si) (***b***)

When examining the fracture microstructure, the laminar phase of Ti_3AlC_2 is observed predominantly in the final part of the sample. Traces have not been detected in the cross section obtained in the initial part of the sample at a distance of 40 mm. Photographs of the fracture microstructure at distances of 100 and 160 mm from the beginning of the sample at the point of contact with the melt bath are shown in Figure 5.

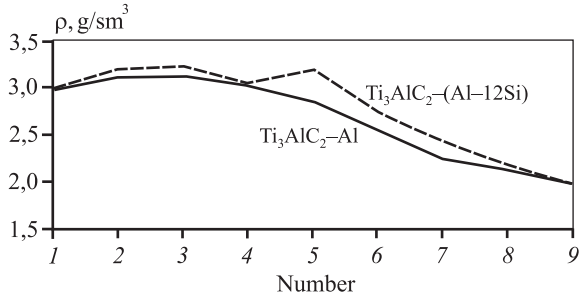

Fig. 4. Density distribution over MAX cermet disk samples

Рис. 4. Распределение плотности по образцам-дискам MAX-керметов

Figure 5, *a* shows equiaxial particles of titanium carbide and a small number of multidirectional plates similar in appearance to Ti_3AlC_2 plates. The latter are predominantly observed in Figure 5, *b* with a small number of rounded TiC particles. It is important to note that at a distance of 160 mm, traces of impregnation are almost absent. The pores in the framework remained unfilled with metal which could lead to a large amount of the observed phase of Ti_3AlC_2. The *X*-ray diffraction patterns of fractures of samples shown in Figure 5 are shown in Figure 6.

According to the height of peaks in Figure 6, *a*, it can be concluded that the main phases in the cermet at a distance of 100 mm are Al and TiC, while Ti_3AlC_2 and $TiAl_3$ are present in a much smaller amount. According to Figure 6, *b*, in a fracture, at a distance of 160 mm, there are no traces of aluminum. Only refractory phases of the TiC and Ti_3AlC_2 framework are observed. According to the results presented, it can be

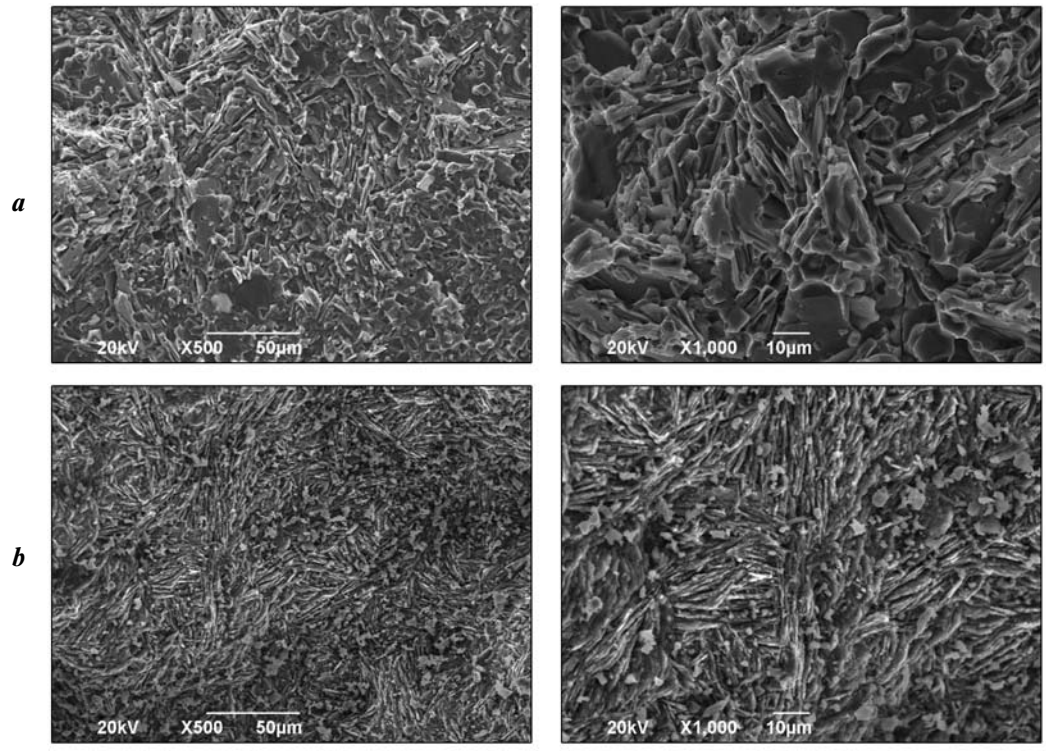

Fig. 5. Fracture microstructure of the sample with target composition Ti_3AlC_2–Al at a distance of 100 mm (***a***) and 160 mm (***b***) from the sample origin

Рис. 5. Микроструктура изломов образца целевого состава Ti_3AlC_2–Al на расстоянии 100 мм (***a***) и 160 мм (***b***) от начала образца

concluded that the aluminum melt impregnating the SHS framework generally destroys the MAX phase of Ti_3AlC_2. This is consistent with the previously obtained data [19]. Therefore, it is not sufficient only to ensure the completion of structure formation of Ti_3AlC_2. The issue of chemical resistance of Ti_3AlC_2 to the incoming aluminum melt superheated during infiltration as a result of heat exchange with the hot SHS framework also needs to be considered.

Study of the microstructure of the MAX cermet sample obtained by infiltration with the Al—12%Si silumin melt was carried out on transverse fractures of the sample at distances of 40, 80, and 120 mm from the melt bath (Figure 7). At all sites a significant number of Ti_3AlC_2 plates is observed. It is important to note that a significant part is in the metal matrix or tightly in contact with it, and the silumin melt has impregnated deeper than pure aluminum.

Fracture diffraction patterns of these sections, shown in Figure 8, revealed the following phase composition: Al, TiC, Ti_3AlC_2, $TiAl_2$, and $TiAl_3$ for sample sections at both 40 mm and 80 mm from the melt bath. Consequently, the addition of 12 % Si to Al contributes to the Ti_3AlC_2 content increase in the impregnated part of the framework. In addition, systematic peaks of $TiAl_3$ and $TiAl_2$ compounds have been detected, and a shift of Al peaks was noted (see Figure 8, *b*). This is due to the presence of silicon in the Al—12%S melt.

Thus, the SHS cermet with the Ti_3AlC_2—Al target composition, obtained by infiltration of pure aluminum, has a different real phase composition: TiC—$TiAl_3$—Al. At the same time, the silumin-based SHS cermet Ti_3AlC_2—(Al—12Si) at the 0—40 mm section, is also another real composition of TiC—$TiAl_3$—(Al—12Si). At the 40—120 mm section, the composition is TiC—Ti_3AlC_2—$TiAl_3$—(Al—12Si). In general, aluminum actively destroys Ti_3AlC_2, and the addition of 12 % Si to it contributes to the preservation of Ti_3AlC_2 in obtaining long-length SHS cermet by spontaneous infiltration of the metal melt. This is probably due to less deinterculation of Al from the MAX phase of Ti_3AlC_2 into the Al—12%Si melt compared to the pure aluminum melt.

The results of hardness studies in cross sections of

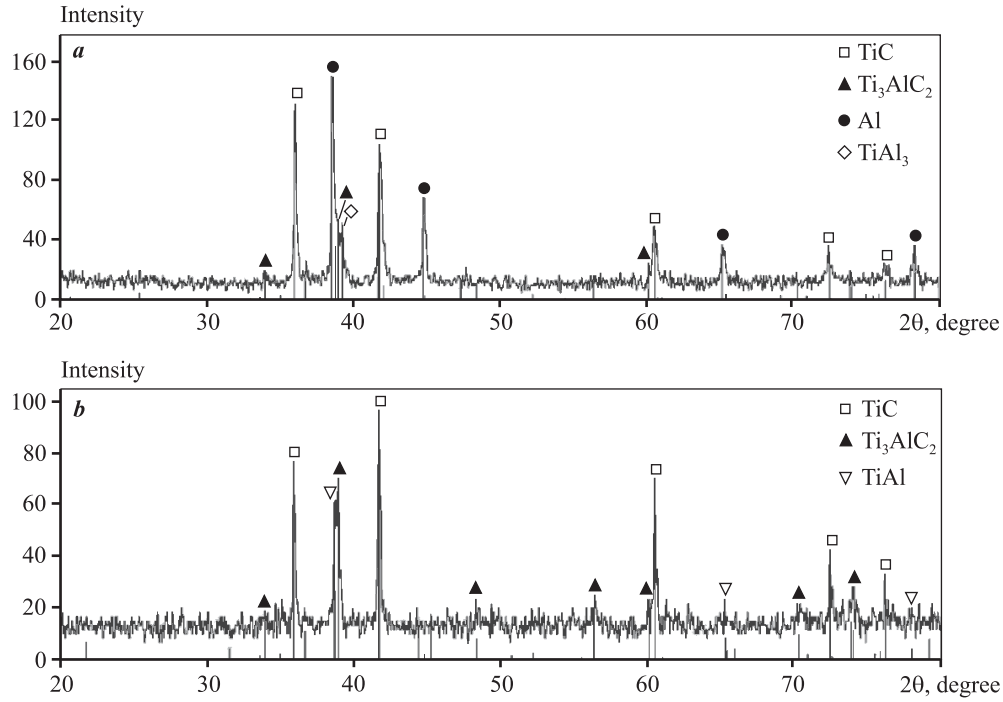

Fig. 6. Fracture XRD patterns of the sample with target composition Ti_3AlC_2–Al at a distance of 100 mm (***a***) and 160 mm (***b***) from the sample origin

Рис. 6. Дифрактограммы изломов образца целевого состава Ti_3AlC_2–Al на расстоянии 100 мм (***a***) и 160 мм (***b***) от начала образца

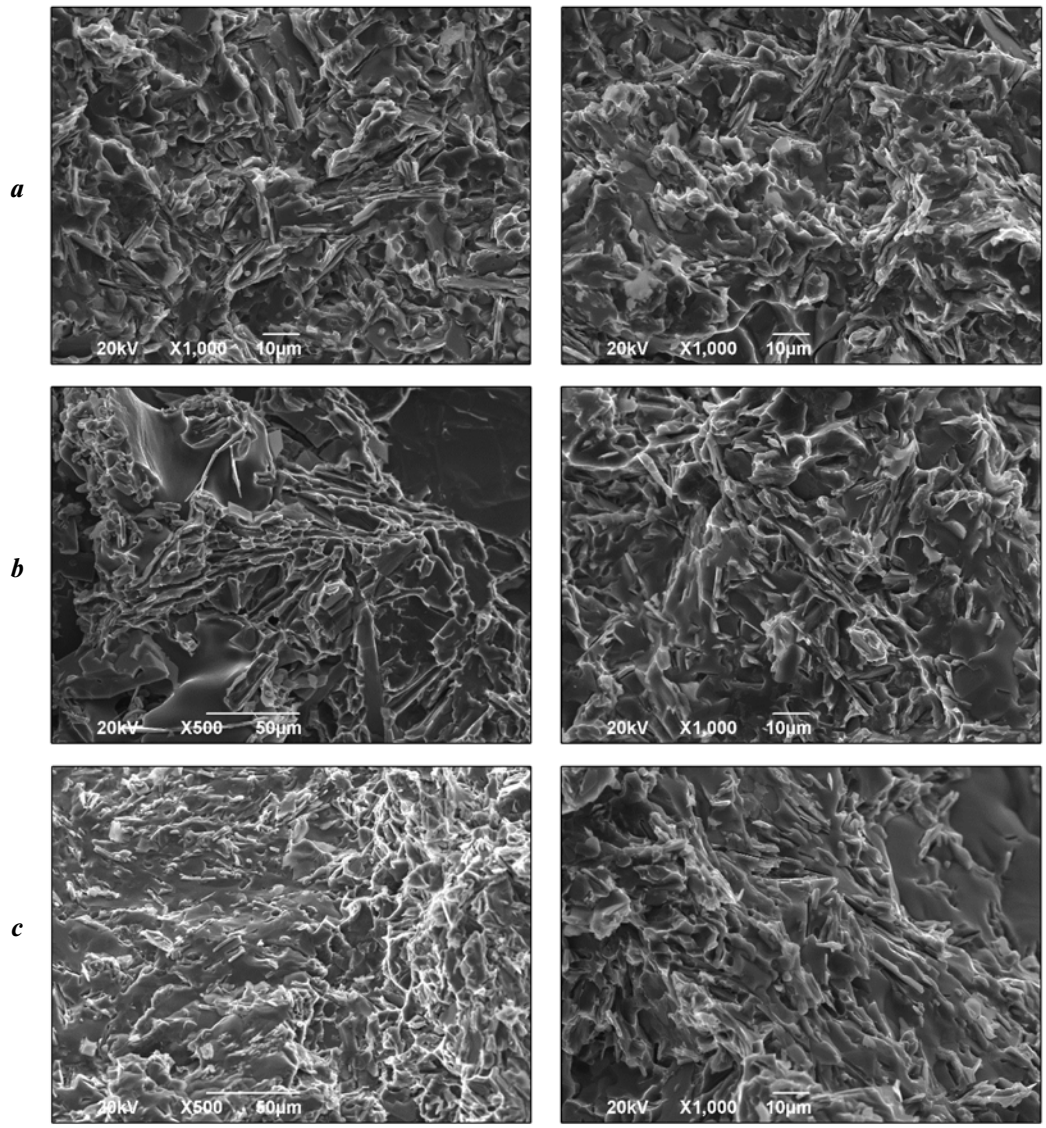

Fig. 7. Fracture microstructure of the sample with target composition Ti_3AlC_2–(Al–12Si) at a distance of 40 mm (***a***), 80 mm (***b***) and 120 mm (***c***) from melt bath

Рис. 7. Микроструктура излома образца целевого состава Ti_3AlC_2–(Al–12Si) на расстоянии 40 мм (***a***), 80 мм (***b***) и 120 мм (***c***) от ванны расплава

the SHS cermets obtained are shown in Figure 9. This shows 3 prints with diameters of 2.63, 2.7 and 2.22 mm after indentation of a steel ball with ∅ 5 mm. After processing the results (prints) of at least 10 tests, the average Brinell hardness value for cermets of the Ti_3AlC_2—Al target composition (in the 100 mm zone) was approximately 640±180 MPa. For Ti_3AlC_2—(Al—12%Si) (in the 80 mm zone) it was 740±310 MPa, which according to the international standard of the hardness value conversion can be estimated conditionally by the values of the strength limit of ~220 and ~250 MPa respectively [22].

The greater hardness of SHS silumin-based cermets can be explained by higher mechanical properties of silumin (about 500 MPa) compared to pure aluminum (200—300 MPa). The significant dispersion of hardness data and relatively low strength of composites can be associated with significant residual porosity, as well as uneven structure across the cross section of the composite as shown in Figure 3. The density of

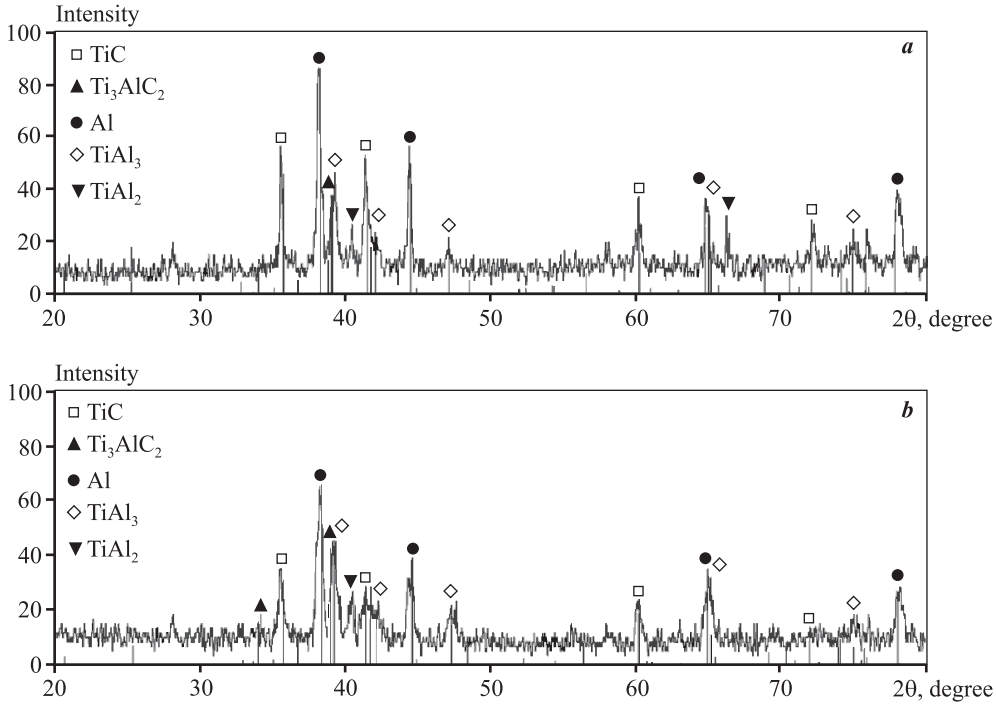

Fig. 8. Fracture XRD patterns of the sample with target composition Ti_3AlC_2–(Al–12Si) at a distance of 40 mm (***a***) and 80 mm (***b***) from melt bath

Рис. 8. Дифрактограммы изломов образца целевого состава Ti_3AlC_2–(Al–12Si) на расстоянии 40 мм (***a***) и 80 мм (***b***) от ванны расплава

Ti_3AlC_2—Al cermets was ρ = 2.88÷3.16 g/cm^3, which, taking into account the phase composition, corresponds to the residual porosity of P = 17.0÷24.6 %. For Ti_3AlC_2—(Al—12%Si) cermets the values are ρ = 3.03÷3.13 g/cm^3 and P = 17.6÷20.3 %. Consequently, the addition of 12 % Si to Al leads to an insignificant decrease in the sample density dispersion and, as a consequence, the residual porosity, contributing to a more uniform distribution of the metal over the SHS framework during infiltration.

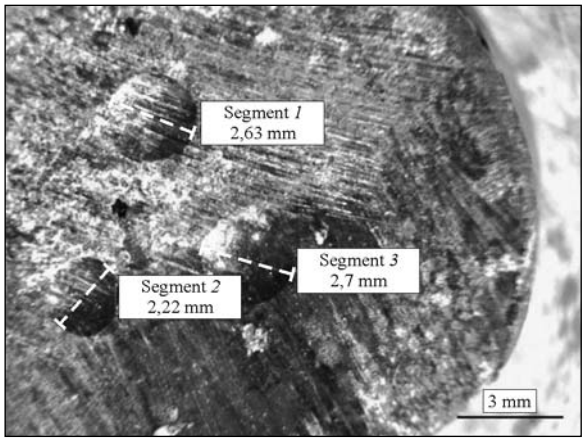

Fig. 9. Indents on the section of SHS cermet with target composition Ti_3AlC_2–(Al–12Si) after hardness test

Рис. 9. Отпечатки индентора на сечении СВС-кермета целевого состава Ti_3AlC_2–(Al–12Si) после испытания на твердость

If we focus on possible applications of MAX phases [2], the developed SHS cermets can be used as light wear-resistant materials. The presence of porosity makes them lighter, and as electrodes for application of wear-resistant coatings. In order to further increase the completeness and depth of infiltration, the temperatures of the SHS framework and aluminum melt need to be increased, while at the same time providing measures to reduce the chemical interaction between them by searching for alloying components.

Conclusion

This study investigated the possibility of applying a new circuit of the previously proposed method, in order

to obtain long-length samples of MAX cermets on an aluminum matrix basis using the SHS process. In this case the synthesis of the Ti_3AlC_2 MAX phase porous framework was carried out by means of the bulk density charge combustion in air atmosphere, followed by spontaneous impregnation with aluminum melt. This provided the pause necessary for the formation of the MAX phase between the passage of the burning and impregnation fronts.

However, instead of MAX samples with the Ti_3AlC_2—Al and Ti_3AlC_2—(Al—12Si), target compositions, the cylindrical samples of SHS cermets with increased dimensions (length up to 110—130 mm and mean diameter of 24 mm) were produced with different real compositions: TiC—$TiAl_3$—Al and TiC—Ti_3AlC_2—$TiAl_3$—(Al—12Si), respectively. In these samples the MAX phase of Ti_3AlC_2 is either practically absent or present in small amounts. This result can be explained by the fact that active destruction occurs during spontaneous infiltration of the Ti_3AlC_2 MAX phase synthesized framework by pure aluminum melt. The addition of 12 % Si to the Al melt promotes an increase in the Ti_3AlC_2 content in the SHS cermet obtained, as well as increasing the total depth of infiltration from ~110 to ~130 mm.

The average hardness value of TiC—$TiAl_3$—Al and TiC—Ti_3AlC_2—$TiAl_3$—(Al—12Si) SHS cermets is *HB* = 640 and 740 MPa, which corresponds conventionally to the ultimate tensile strength of the obtained materials of about ~220 and 250 MPa, respectively. In the case of the TiC—$TiAl_3$—Al sample, the density is 2.88—3.16 g/cm^3, and the residual porosity is 17.0—24.6 %, and for the TiC—Ti_3AlC_2—$TiAl_3$—(Al—12Si) cermet these parameters are equal to $\rho = 3.03 \div 3.13$ g/cm^3, $P = 17.6 \div 20.3$ %.

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