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## Interparticle Interactions during Consolidation of $\text{Ti}_3\text{SiC}_2$ -Cu Powders Influenced by Preliminary Mechanical Milling\*

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### Abstract

Mechanical milling is widely used for the purpose of efficient mixing of the components of particle-reinforced composite materials, which are further obtained in a bulk form by consolidation of the milled powder mixtures. Using the  $\text{Ti}_3\text{SiC}_2$ -Cu system as an example of a metal matrix composite with a ductile matrix and a reinforcement phase prone to chemical interaction with the matrix at elevated temperatures, we show that the effect of the preliminary mechanical milling of the components is seen not only in the uniformity of distribution of the reinforcing particles in the matrix but also in the consolidation behavior of the powders. The influence of the presence of composite agglomerates in the milled mixture on the processes induced by heating during consolidation is demonstrated by detonation spraying of the mechanically milled and mixed  $\text{Ti}_3\text{SiC}_2$ -Cu powders in comparative experiments and Spark Plasma Sintering of the  $\text{Ti}_3\text{SiC}_2$ -Cu agglomerates of different morphology. Interparticle interactions that are affected by the presence/absence of composite agglomerates and their morphology are the interfacial chemical reactions, the degree of transformation and melting of the copper matrix in the contact regions.

### INTRODUCTION

The powder preparation stage of powder metallurgy processing of metal matrix composites often includes mechanical milling of the mixtures aimed at mixing the particles of the reinforcement with those of the matrix phase [1–4]. As the particles of the reinforcement should be distributed in a metal matrix as uniformly as possible to achieve better mechanical properties and isotropy of the composite, those conditions of mechanical milling are chosen that result in the plastic deformation of the matrix particles, which are usually larger than the particles of the reinforcement. Due to repeated cold welding and fracturing, the product of mechanical milling consists of dense composite

agglomerates [5]. The morphology of the composite agglomerates depends on the milling conditions, composition and the use of process control agents.

In this work, we show that the uniformity of distribution of reinforcing particles in the consolidated composite is not the only consequence of the preliminary mechanical milling of the powder mixtures. We use the  $\text{Ti}_3\text{SiC}_2$ -Cu system as an example of a metal matrix composite with a ductile matrix and a reinforcement phase capable of chemically interacting with the matrix. Titanium silicon carbide,  $\text{Ti}_3\text{SiC}_2$ , belongs a class of MAX phases, which are carbides and nitrides with a general formula  $\text{M}_{n+1}\text{AX}_n$ , where M is an early transition metal, A is an element from IIIA or IVA group and X is carbon or nitrogen [6]. In contact with metals, MAX phases are unstable at elevated temperatures; chemical interactions between metals and MAX phases result in deintercala-

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tion of the A element and its dissolution in the metal or formation of an intermetallic compound with the metal. From a practical viewpoint,  $\text{Ti}_3\text{SiC}_2$ -Cu composites are promising materials for electrical applications as sliding contacts and current collector inserts. In this study, mechanically milled and mixed  $\text{Ti}_3\text{SiC}_2$ -Cu powders were detonation sprayed in comparative experiments and agglomerates of different morphology produced by milling were Spark Plasma Sintered (SPS-ed). By studying the interparticle interactions during temperature-assisted and electric current-assisted consolidation of the  $\text{Ti}_3\text{SiC}_2$ -Cu powders, it was possible to demonstrate that the processes concurrent with consolidation, such as chemical interaction at the interface and local melting of the copper matrix, are influenced by the structure of the composite mixture. During consolidation assisted either by heating of the powders by high-velocity gas flows [7, 8] or by electric current under pressure [9], the influence of the structure of the composite powder mixture on the interparticle interactions is exerted through changing the extent of particle heating, including local heating.

## EXPERIMENTAL

Titanium silicon carbide  $\text{Ti}_3\text{SiC}_2$  was synthesized from elements in the powder mixtures of Ti (99 % purity), Si of semiconductor purity and amorphous carbon (lampblack, PM-15). The mixtures were mechanically milled and ignited to initiate a reaction of self-propagating high temperature synthesis. The synthesized  $\text{Ti}_3\text{SiC}_2$  was mechanically milled and sieved to eliminate agglomerates larger than 40  $\mu\text{m}$ . The composite powders were prepared by milling of the  $\text{Ti}_3\text{SiC}_2$  and Cu (PMS-1, electrolytic, 99.7 %) powder mixtures (Fig. 1). The content of  $\text{Ti}_3\text{SiC}_2$  in the mixtures was 5–20 vol. %. The composite powders were sieved through a sieve with a size of openings of 71  $\mu\text{m}$  to separate a coarse fraction unsuitable for the detonation spraying. An AGO-2 planetary ball mill with water-cooled milling vials was used with a ball acceleration of 200  $\text{m/s}^2$ . The powder mixtures were loaded in the milling vials in a glove box under an atmosphere of high-purity argon.

Detonation spraying uses heating and acceleration of powder particles toward substrates

by the products of gaseous detonation [7]. In Computer-Controlled Detonation Spraying (CCDS) [8], the temperature and velocity of the sprayed particles as well as the chemistry of the spraying environment can be controlled by varying the fuel to oxidizer ratio and the amount of an explosive mixture used for the shots of the detonation gun. The coatings were deposited using a CCDS2000 facility (Lavrentyev Institute of Hydrodynamics of SB RAS, Novosibirsk). The barrel of the detonation gun was 1000 mm long and 20 mm in diameter. The spraying distance was 100 mm. Air was used as a carrier gas. Spraying was performed using different compositions of acetylene-oxygen mixtures corresponding to  $\text{O}_2/\text{C}_2\text{H}_2$  molar ratios of 1.1 and 1.5. The explosive charge was 30 and 40 % of the barrel volume. Spark Plasma Sintering was carried out using a SPS Labox 1575 apparatus (Japan). The sample was heated at a rate of 50  $^\circ\text{C}/\text{min}$ . The maximum SPS temperature was 850  $^\circ\text{C}$ . When this temperature was reached, the process was stopped and the sample was allowed to cool down to room temperature. At the beginning of the sintering cycle, a uniaxial pressure of 5 MPa was applied to ensure reasonable contact conditions in the punch-powder sample assembly and a pressure of 40 MPa was applied to the sample when the SPS temperature reached 300  $^\circ\text{C}$ . Further details of the powder synthesis, milling and consolidation by detonation spraying and SPS can be found in [10, 11].

The X-ray diffraction (XRD) patterns of the powders, detonation sprayed coatings and SPS-ed compacts were recorded by means of a D8 ADVANCE powder diffractometer (Bruker AXS) equipped with a one-dimensional Lynx-Eye detector and using  $\text{CuK}_\alpha$  radiation. XRD phase analysis was performed using ICDD PDF-4+ database (Release 2011). The morphology of the powders and microstructure of the coatings and SPS-ed compacts were studied using a Hitachi-Tabletop TM-1000 Microscope in the backscattered electron imaging mode.

## RESULTS AND DISCUSSION

As can be seen from Fig. 1, the  $\text{Ti}_3\text{SiC}_2$  starting powder contained a significant fraction of fine particles in the micrometer and submic-

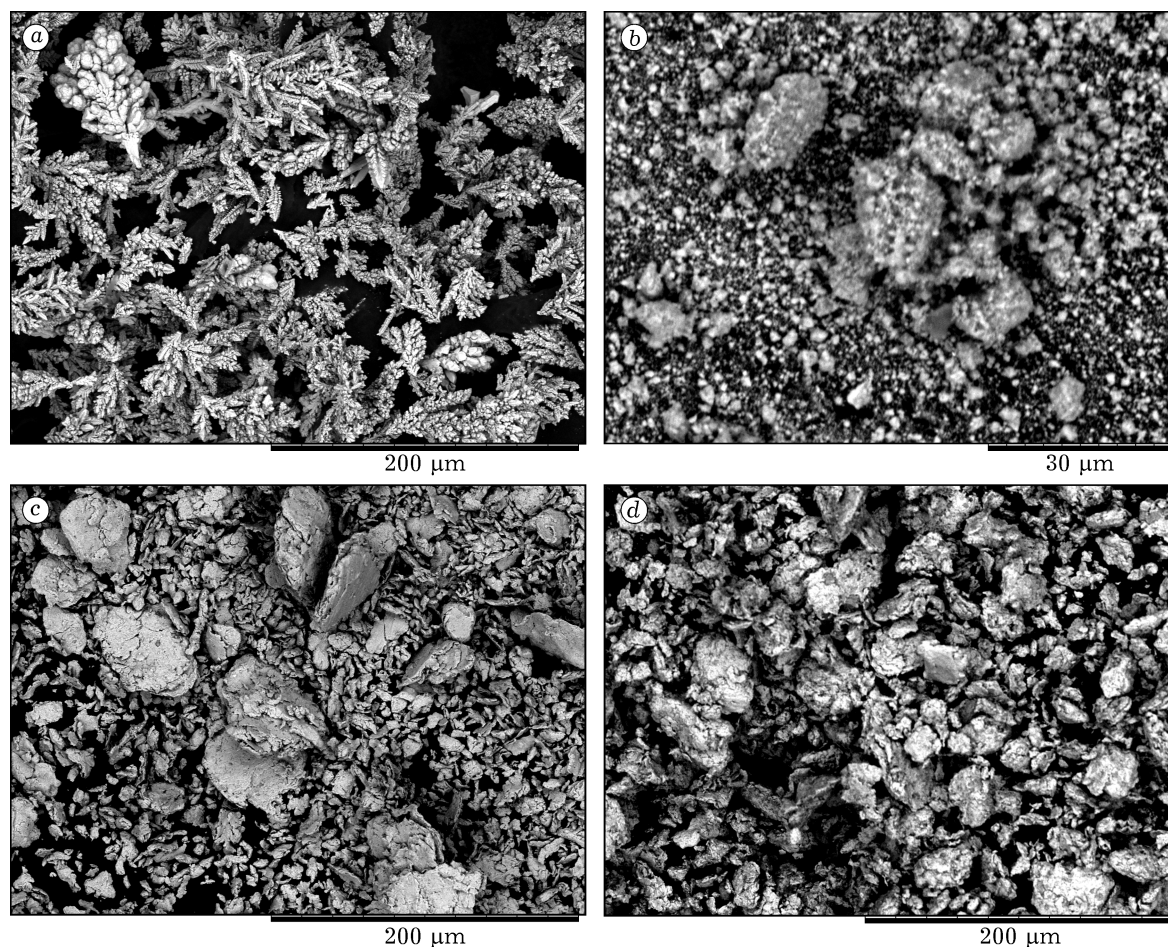


Fig. 1. Morphology of the starting powders and  $\text{Ti}_3\text{SiC}_2$ -Cu composite agglomerates produced by mechanical milling: a - electrolytic copper powder; b -  $\text{Ti}_3\text{SiC}_2$ -based powder synthesized by self-propagating high-temperature synthesis, milled and sieved; c - 5 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu; d - 20 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu.

rometer range. At the same time, agglomerates several tens of microns in size were also present. When mechanically milled, Cu and  $\text{Ti}_3\text{SiC}_2$  formed composite agglomerates, whose morphology and size depended on the composition of the mixture: in the 5 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu mixture, flaky or platelet-shaped agglomerates with a wide size distribution were obtained, while in the 20 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu mixture under the same milling conditions, agglomerates with a narrower size distribution formed, whose morphology can be better described as irregular (see Fig. 1).

We compared the behavior of the mechanically milled powders of the 20 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu composition and those mixed in a mortar during detonation spraying under constant conditions in terms of explosive charge and  $\text{O}_2/\text{C}_2\text{H}_2$  ratio. Cross-sections of the coatings shown in Fig. 2 demonstrate dramatic differences in the

microstructure of the coatings produced from the milled and non-milled mixtures. The most obvious difference is the distribution of the  $\text{Ti}_3\text{SiC}_2$  particles: in the coatings produced from the milled mixture, no agglomerates of the reinforcing phase can be seen; rather, a very uniform distribution of the  $\text{Ti}_3\text{SiC}_2$  particles in the copper matrix is achieved. Another observation is the earlier onset of the reaction between the phases in the non-milled mixture (Fig. 3), which is normally not to be expected when milled and non-milled mixtures are conventionally heated in a comparative experiment. As can be seen from the XRD patterns of the coatings, the coating deposited at an explosive charge of 30 % and  $\text{O}_2/\text{C}_2\text{H}_2 = 1.1$  from the milled powders preserves the phase composition of the powder. The non-milled mixture, however, experiences partial transformation in

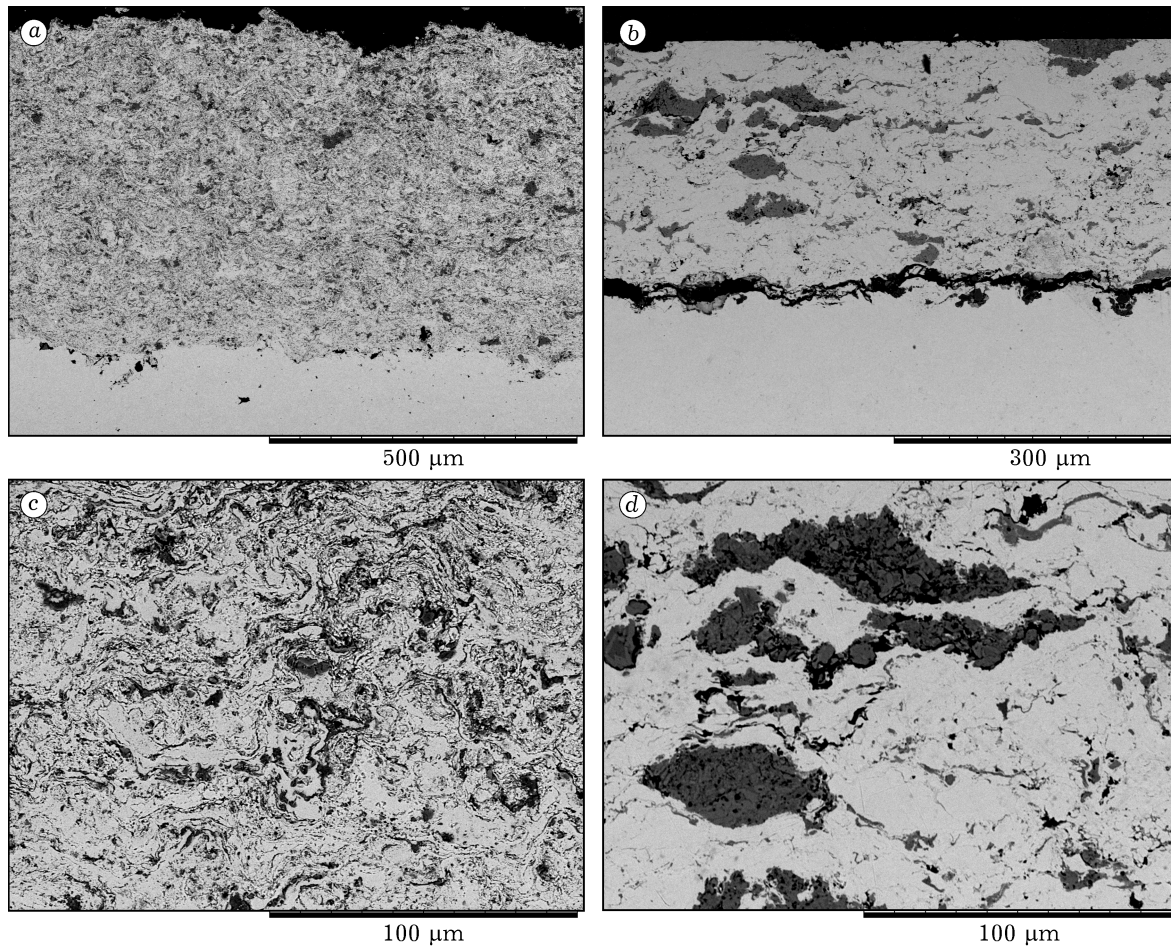
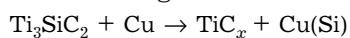


Fig. 2. Cross-sections of the coatings produced by detonation spraying of 20 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu powders at explosive charge 30 %,  $\text{O}_2/\text{C}_2\text{H}_2 = 1.5$ : a, c - mechanically milled mixture; b, d - mixed in a mortar.

these conditions with  $\text{TiC}_x$  being the reaction product. According to [12], the interaction between Cu and  $\text{Ti}_3\text{SiC}_2$  starts at 900 °C. Depending on the relative content of the reacting phases, Si forms either a solid solution in copper or a Cu-Si compound. In the composite mixtures studied in this work, the content of Si in Cu did not exceed 5 at. % assuming full decomposition of the MAX phase, which is well below the maximum solubility of Si in Cu. Therefore, as fast cooling is characteristic of both detonation spraying and SPS, metastable solid solutions Cu(Si) are likely to form as a result of the interfacial interaction between  $\text{Ti}_3\text{SiC}_2$  and Cu according to the following reaction:



The characteristics of the heating process of the powders by the detonation products depend on the particle size [13]. When a simple mixture is sprayed, the Cu and  $\text{Ti}_3\text{SiC}_2$  parti-

cles are heated separately, and, therefore, fine  $\text{Ti}_3\text{SiC}_2$  particles can get overheated. Upon deposition they can react with copper locally even though the average temperature of the copper particles is less than 900 °C. In higher-temperature conditions of spraying (with increasing explosive charge or oxygen content in the  $\text{O}_2 + \text{C}_2\text{H}_2$  mixture), the coatings produced from the milled mixtures indicated full transformation of  $\text{Ti}_3\text{SiC}_2$  into  $\text{TiC}_x$ , as can be concluded from the XRD patterns (see Fig. 3, a). In the non-milled mixtures, however, the reaction is not complete even at higher temperatures due to the presence of  $\text{Ti}_3\text{SiC}_2$  agglomerates and a limited interfacial area between  $\text{Ti}_3\text{SiC}_2$  and Cu. In the non-milled mixture, a reflection that does not belong to either  $\text{Ti}_3\text{SiC}_2$ ,  $\text{TiC}_x$  or Cu phases has been identified in the XRD patterns (see Fig. 3, b), which may be indicative of partial oxidation of  $\text{Ti}_3\text{SiC}_2$  during spraying when the

particles are not “protected” by the copper matrix. Partial oxidation of MAX phases is known from the data reported by other researchers [14] and is a major problem of thermal spraying of these compounds.

Worth noting is a high quality of the interface between the coating and the copper substrate in the case of spraying of the mechanically milled mixture (see Fig. 2, *a*). A possible explanation of the inferior substrate/coating interface in the case of spraying of the non-milled mixture (see Fig. 2, *b*) is the erosion effect caused by the hard ceramic particles reaching the substrate separately from the ductile copper matrix, especially by the  $Ti_3SiC_2$  agglomerates. These results show that when composite (multimaterial) coatings are produced [15], the mixed powders and the composite agglom-

erates produced by mechanical milling may behave differently in terms of interparticle interactions, including chemical interactions; therefore, the “milled” and “non-milled” alternatives for composite mixtures can be considered to reach the desired microstructure/property combination.

In sintering of powders, interparticle interactions include the contact and neck formation and chemical reactions induced by heating. Sintering of the mechanically milled  $Ti_3SiC_2$ -Cu composite powders of different morphology by passing electric current under pressure revealed microstructural features of the compacts characteristic of certain morphology of the agglomerates. The flaky/platelet morphology of the composite powder facilitated densification, which is seen from Fig. 4, *a* showing a fracture

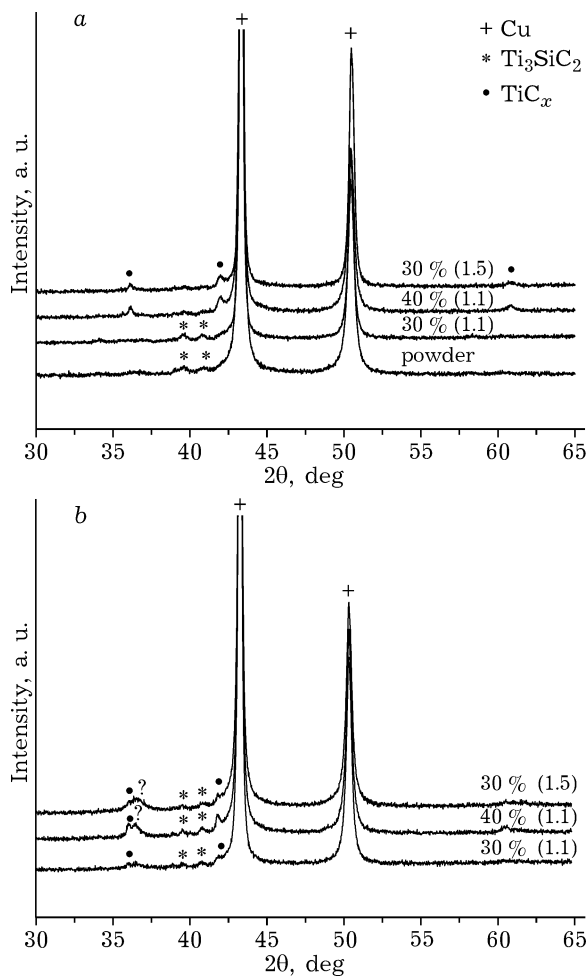


Fig. 3. XRD patterns of the coatings produced by detonation spraying of 20 vol. %  $Ti_3SiC_2$ -Cu powders: *a* – mechanically milled mixture, *b* – mixed in a mortar.

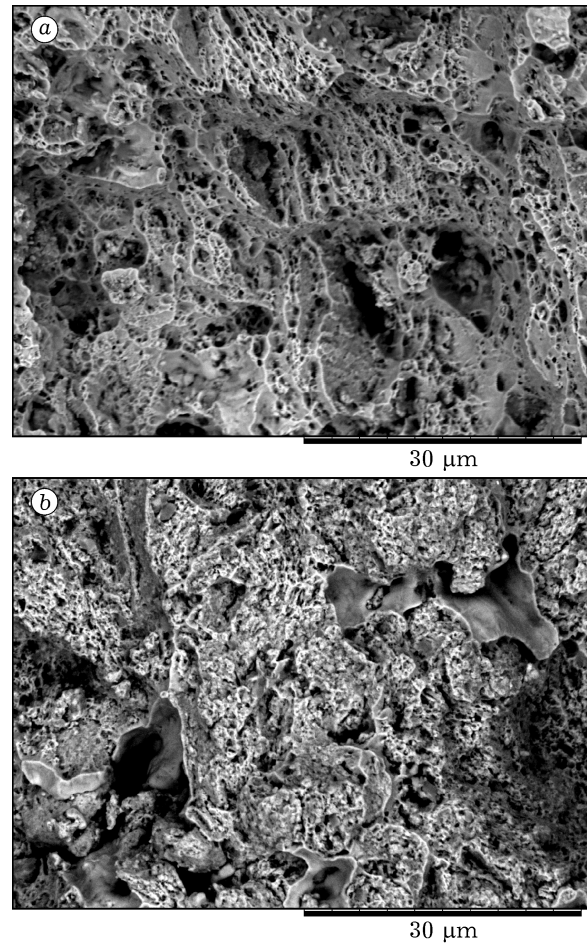


Fig. 4. Cross-sections of the compacts produced by SPS of 5 vol. %  $Ti_3SiC_2$ -Cu (*a*) and 18 vol. %  $Ti_3SiC_2$ -Cu (*b*) mechanically milled powders.

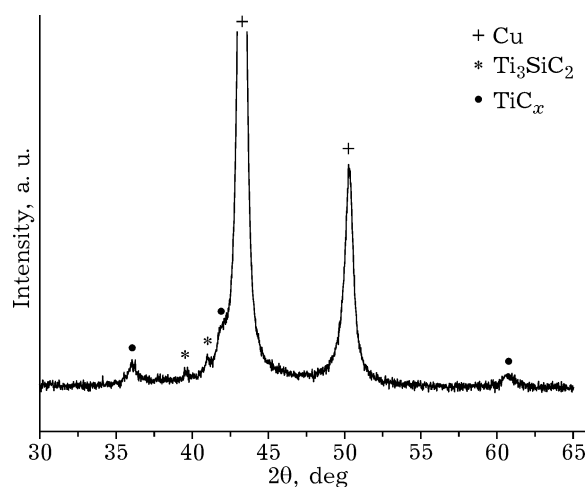


Fig. 5. XRD pattern of the compact produced by SPS of 18 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu mechanically milled powder.

surface of the 5 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu. The consolidated composite is 92 % dense and shows features of ductile fracture indicating the established bonding between the agglomerates. In SPS-ed compacts obtained from the 18 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu particles of irregular shape by consolidation at the same temperature and pressure, areas of refrozen melt were found (see Fig. 4, b). Local melting of the copper matrix is due to a higher contact resistance between the particles of irregular morphology than between platelets arranging themselves parallel to each other with their flat side normal to the pressure direction. The result of a higher contact resistance is a more intense Joule heating of the interparticle contacts. The XRD pattern of the 18 vol. %  $\text{Ti}_3\text{SiC}_2$ -Cu compact (Fig. 5) shows partial transformation of  $\text{Ti}_3\text{SiC}_2$  into  $\text{TiC}_x$ , which is consistent with the local occurrence of the reaction in the overheated contact zones between the composite particles.

## CONCLUSIONS

We have shown that the structure of the  $\text{Ti}_3\text{SiC}_2$ -Cu composite mixture affects the processes induced by heating of the material during its consolidation. During detonation spraying of the  $\text{Ti}_3\text{SiC}_2$ -Cu composite mixture prepared by mixing in a mortar, the reaction between  $\text{Ti}_3\text{SiC}_2$  and Cu starts in milder condi-

tions of spraying than the same reaction in the mechanically milled mixture. This can be rationalized if overheating of the fine  $\text{Ti}_3\text{SiC}_2$  particles contained in the starting powder, and, consequently, in the mixture prepared by mixing in a mortar, is taken into account. While in mechanically milled mixture the reaction, if initiated, led to full transformation, in the mixtures mixed in a mortar, untransformed  $\text{Ti}_3\text{SiC}_2$  was present due to agglomeration and a reduced interfacial area between  $\text{Ti}_3\text{SiC}_2$  and Cu. During SPS, flaky morphology of the composite powder facilitated densification. In SPS-ed compacts obtained from particles of irregular shape at the same temperature, local melting of the copper matrix was detected as a result of a higher contact resistance between the particles. Thus, by studying the interparticle interactions during detonation spraying and electric current-assisted consolidation of the  $\text{Ti}_3\text{SiC}_2$ -Cu powders, we have demonstrated that the consolidation-accompanying processes, such as chemical interactions at the interface and local melting of the matrix, are influenced by the structure of the composite mixture, which can be altered by preliminary mechanical milling.

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