

Mechanochemical Methods for the Synthesis of Metal-Ceramics-Polytetrafluoroethylene Composite Materials

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Abstract

Solid-phase mechanochemical methods for the synthesis of new materials, metal-fluoropolymer and metal-ceramics-fluoropolymer composites have been developed. Composite materials possessing high electric conductivity, low friction coefficient and mechanical attrition resistance were synthesized from W–Cu, WC–Cu, and Cu–TiB₂ and ultrafine polytetrafluoroethylene (UPTFE) systems. It is demonstrated that thermal stability of mechanically processed pure UPTFE differs from that of the PTFE component of mechanocomposites and depends on the nature of the main component of the composite.

INTRODUCTION

Solid-phase mechanochemical methods for the synthesis of materials from metals have been actively developed during the last decades. In contrast to high-temperature or plasma, laser, and radiation methods, these are accessible, economic, and environmentally friendly technologies [1]. This work deals with the results of solid-phase studies aimed at synthesis of promising electrocontact and electroerosion materials operating under extreme conditions including sliding electric contact conditions.

Copper-containing composites are traditional electrocontact and electroerosion materials. Among these are materials based on the W–Cu system of immiscible metals and copper-containing cermet. The absence of chemical interaction in immiscible systems under high temperature conditions makes it possible to approach the initial conditions during system relaxation. Erosion resistance of these materials increases with reduced grain size, and the friction coefficient may be decreased by incorporating components with low friction coefficients in the material. Using ultrafine

polytetrafluoroethylene (UPTFE) as a component of this kind [2] has stimulated the development of synthetic methods and investigations of the properties of metal-fluoropolymer composites as a new class of materials.

IMMISCIBLE METALS—ULTRAFINE POLYTETRAFLUOROETHYLENE COMPOSITES

Materials based on immiscible metals with positive mixing heats are traditionally used under conditions of high energy flux dissipation, for example, in electroerosion devices or in mechanical frictional brake blocks. Metal-fluoropolymer composites are interesting from the viewpoint of their potential applications as materials for sliding electric contacts. The high erosion strength of these materials is due to the metals not interacting with each other at elevated temperatures; and fluoropolymer provides the low friction coefficient.

As is known [3], W–Cu composites are widespread materials for electric contacts,

switches, and electrodes operating in both vacuum and insulators (SF_6). Owing to the high thermal and electric conductivity of copper and the high-temperature stability and low thermal expansion coefficient of tungsten, W-Cu composites possess a unique combination of properties. Varying the microstructure and the tungsten content, selecting proper additives that are soluble (Ni or Sb) or insoluble (Mo) in copper, and using the hardening properties of ceramic phases – oxides, nitrides and carbides, one can obtain composites with optimum properties for specific applications.

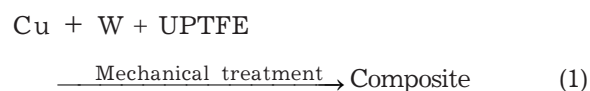
Because of the mutual insolubility of metals in tungsten-copper systems, homogeneous materials are difficult to obtain. For compacting the W-Cu system, it is important to provide high density close to theoretical. For this, one can use solid- and liquid-phase sintering, as well as melt infiltration.

The melt infiltration procedure was recently considered optimal for synthesizing high-density structures [4]. However, the development of mechanical alloying theory and applications made it possible to obtain homogeneous high-density composites using liquid- and solid-phase sintering procedures [5, 6].

For mechanical alloying, a mixture of the starting tungsten and copper powders is treated in a ball grinder. For all mechanical alloying and mechanical treatment experiments carried out in this work, we used an AGO-2 planetary ball grinder (acceleration 60 *g*, steel drums and balls, balls mass 200 g, powder charge mass 10 g, UPTFE mass fraction 0.5–1.0 %, treatment time 1–5 min). Treatment was performed in an argon atmosphere.

Presently, there is no consensus of opinion concerning the mechanism of mechanical alloying [7–10]; it is obvious, however, that mechanical treatment of mixtures of some metals promotes formation of homogeneous materials with submicron [5] and occasionally nanosized [11] particles and improves the caking capacity of the composite [5, 6].

Synthesis of a composite material is described by the following scheme:



Ultrafine polytetrafluoroethylene [2] performs a number of functions during synthesis. As is known, for mechanical treatment of individual powders and powder blends, one can use agents that control the grinding process [12]. Figure 1 shows SEM images of composite particles. Mechanical treatment of copper and tungsten powders gives rise to large agglomerates several hundreds microns in size (see Fig. 1, *a*). If PTFE additive with mass fraction of 1 % is used, the particle size of the composite is 30–60 μm (see Fig. 1, *b*). The uniform distribution of UPTFE within the composite enhances compressibility of the material through reduction of friction between particles.

Using composite materials for creating surface layers by spraying in a gas stream entails some additional requirements to the powder material. It has been demonstrated experimentally that the conditions employed

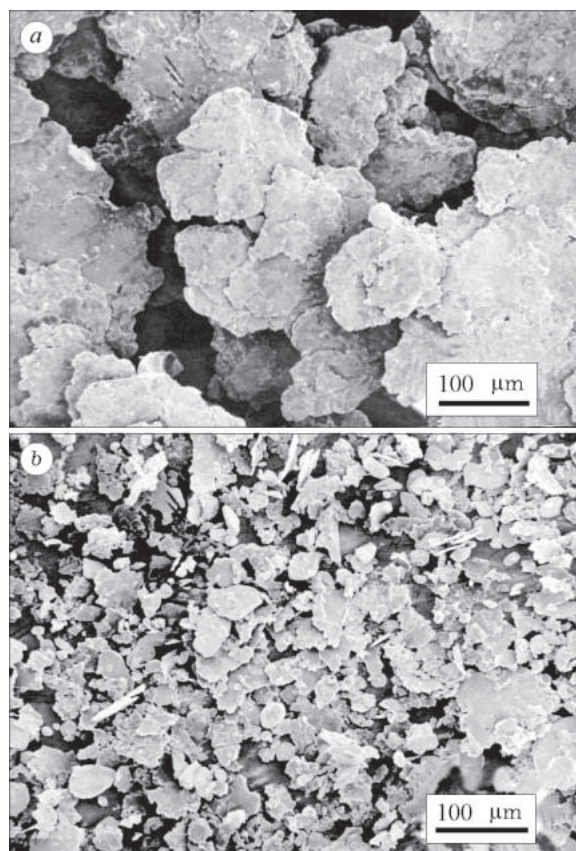


Fig. 1. Micrograph of W-Cu 30 % composite particles obtained by mechanical treatment of a mixture of W and Cu powders in an AGO-2 planetary ball grinder without a PTFE additive (*a*) and the same for composites doped with PTFE (*b*).

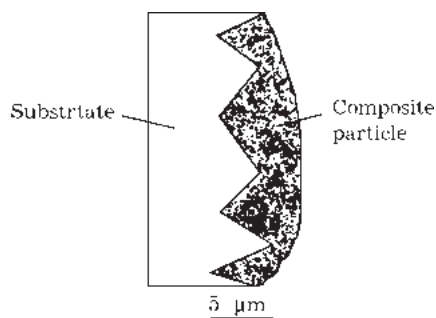


Fig. 2. Schematic diagram of contact between the composite particle and the surface of a rough substrate.

during cold gas dynamic spraying cause effective interaction of particles with the surface if the particle size is 10–60 μm . Larger particles do not have enough time to accelerate to an adequate speed, while smaller particles are reflected from the dense gas layer near the sprayed-on surface. The schematic diagram of particle contact with the surface of a rough substrate (typically as rough as 1–5 μm) is presented in Fig. 2. Obviously, the composite constituents should be smaller. Mechanochemically obtained composite powders meet the above requirements to size and structure.

Adhesion of a sprayed-on particle can be achieved through melting in the zone of roughness tips. With increasing UPTFE content in the particle, friction in this zone decreases, and so does adhesion of the sprayed-on particle. The optimum mass fraction of UPTFE in the composites that provides low friction coefficient and high adhesion of the coating was determined experimentally (0.5–1.0 %).

The results of studies on the friction coefficient of the W-Cu composite coating are given in Fig. 3. The high initial value of the friction coefficient gradually decreases to a steady-state value. This is caused by the rearrangement of the initial structure of the layer due to mechanical smoothing of the surface microrelief and UPTFE distribution over the surface of the rubbing layer. It can be seen that the friction coefficient is 0.08–0.10, which is close to the value typical for bulk fluoroplastic material, 0.05 [13].

Electrical resistance of this coating differs from that of a coating without UPTFE by no more than 5 %. Reduction of the friction

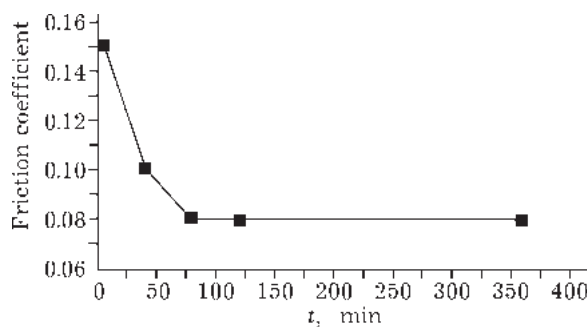


Fig. 3. Friction coefficient of W-Cu coating containing 1 % PTFE and ShKh15 hardened steel in the absence of liquid lubricant.

coefficient for composites with UPTFE is especially important in materials useful in manufacturing sliding electric contacts.

Thus the suggested procedure makes it possible to obtain materials whose friction coefficient approach that of fluoroplastic, while electrical resistance approaches that of metallic copper.

CERMET-ULTRAFINE POLYTETRAFLUOROETHYLENE COMPOSITES

WC-Cu systems are of interest from the viewpoint of incorporating a fluoropolymer component to reduce the friction coefficient of the compact material. The carbide phase imparts them enhanced wear resistance. The smaller the carbide grain, the higher the lifetime of the contacting material [14]. Mechanical grinding affords particles of the order of 1 μm in size. Therefore, an alternative approach has been suggested [15], namely, mechanochemical synthesis of tungsten carbide in a copper matrix.

Mechanical treatment of a mixture of W, C and Cu powders enables one to obtain a precursor whose subsequent thermal treatment leads to synthesis of tungsten carbide. The copper matrix is not an inert diluent, but plays a specific part. Kinetic studies of carbide formation in precursors of different compositions have been carried out [15], and the optimum time of mechanochemical treatment to yield the maximum content of the carbide phase has been determined for each composition.

This approach may be applied to synthesis of polymer-containing composite materials according to scheme (2).

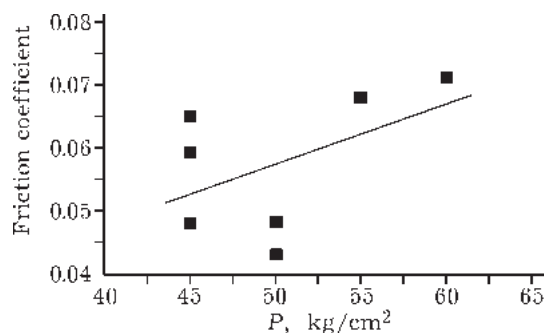
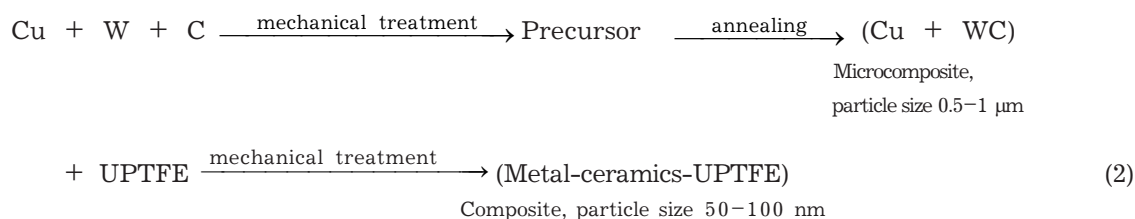


Fig. 4. Friction coefficient of W-Cu coating obtained by cold gas-dynamic spraying.

A layer of the metal-ceramics-UPTFE powder composite applied by cold gas-dynamic spraying to an aluminium substrate ensures high electric conductivity and low friction coefficient. The results of friction studies for this system are presented in Fig. 4. Measurements of the friction coefficient were performed at the stage of steady-state friction. As can be seen, the friction coefficient is close to the value for bulk fluoroplastic and increases slightly with the load. Materials of this type hold much promise for application in sliding contacts of electrotransport.

Cu-TiB₂-ULTRAFINE POLYTETRAFLUOROETHYLENE NANOCOMPOSITES

Cu-TiB₂ is an attractive composite because of the successful combination of the physical properties of its constituent phases. The high

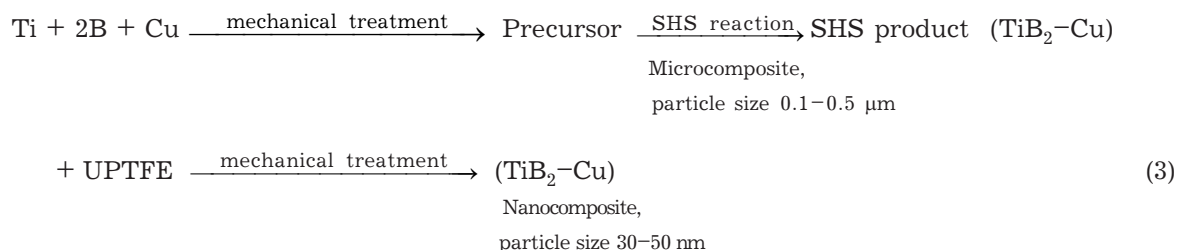
thermal and electric conductivity of copper make it indispensable for use in electric contacts. However, its low strength at high temperatures necessitates the design of composites devoid of these limitations but preserving the valuable properties of metallic copper. Titanium diboride exhibits high melting point, hardness, wear resistance, and significant thermal and electric conductivities [16]. Therefore, when titanium diboride is incorporated into the metal matrix, the rigidity, hardness, and wear resistance of the composite increase, while its thermal and electric conductivities slightly decrease.

During the reaction between titanium and boron, heat emission is so high that the reaction can occur as self-propagating high-temperature synthesis (SHS) [17].

A procedure for the synthesis of the Cu-TiB₂ nanocomposite has been worked out previously [18]. To synthesise a polymer-containing nanocomposite, UPTFE powder is added at the stage of mechanical treatment of the product of the SHS reaction (scheme (3)).

A TEM image of the microstructure of the Cu-TiB₂-UPTFE mechanocomposite is presented in Fig. 5. It can be seen that the size of crystallites is 30–50 nm with components distributed homogeneously.

Importantly, thermal stability of mechanically processed pure UPTFE differs from that of PTFE in mechanocomposites and



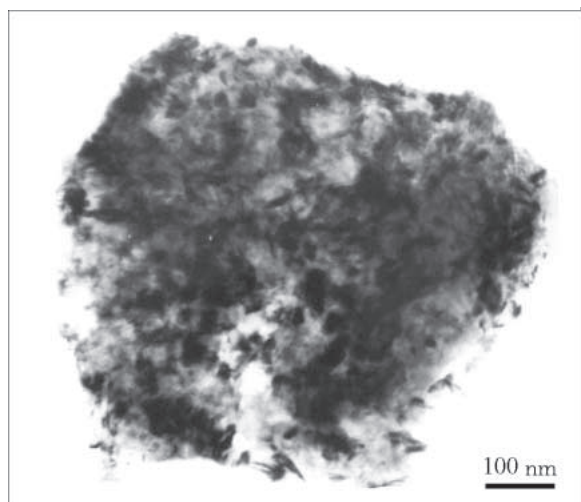


Fig. 5. TEM image for TiB_2 -Cu nanocomposite with 60 % UPTFE.

depends on the nature of the main component of the composite. As can be seen from Fig. 6 (curve 1), at elevated temperatures mass loss of UPTFE occurs in two stages. In the temperature range 25–325 °C, sublimation takes place; around 325 °C, fluoroplastic starts to melt and decompose. The physicochemical transformations of UPTFE during mechanical treatment with the components of the fusion mixture should result in changes on the thermogravimetric (TG) curve of heating for mechanically activated samples. Sublimation of fluoroplastic depends on the size of the fluoroplastic macromolecule and on the amount of intermolecular interaction between the macromolecule and the fluoroplastic matrix.

Increased slope of the TG curve is indicative of polymer chain splitting and disordering in the solid fluoroplastic, weakening the intermolecular bonds. For a mixture of fluoroplastic and the components of the fusion mixture, decreased slope of the TG curve in comparison with the initial curve (see Fig. 6, curve 1) suggests that stronger bonds formed between the fluoroplastic molecules and the surface of the formulation component.

The time of mechanical activation of UPTFE with Cu, B and Ti was 2 min. Because of the difference in the dimensions of the starting powders, the mass of the UPTFE dopant was chosen: from 0.5 % for Ti to 1 % for Cu. The mass of the UPTFE dopant was determined with

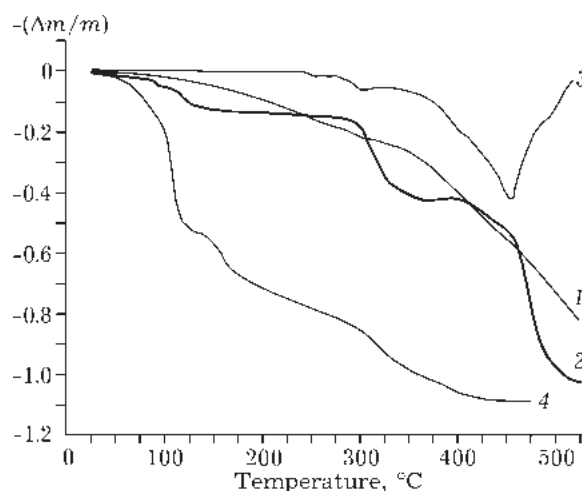


Fig. 6. Thermograms of mechanically activated samples: 1 – pure UPTFE; 2–4 – UPTFE mixtures with Cu (2), Ti (3), B (4).

the following assumptions. The number of adsorption sites was assumed to be 10^{13} cm^{-2} . Because the number of surface copper atoms is $1.6 \cdot 10^{15}$, this implies that one of 100 surface copper atoms can be bonded to the sorbate molecule. The second assumption concerns the orientation of the sorbed UPTFE oligomers. It is believed that tribo-reagent molecules (in our case, UPTFE oligomer) are preferably perpendicular to the surface [19]. The dimensions of the copper particles are $\sim 1 \mu\text{m}$ for electrolytic copper and $\sim 60 \mu\text{m}$ for the copper powder obtained by a different procedure. For titanium powder, particle size is $\sim 10 \mu\text{m}$. Based on particle size, we can estimate the specific surface ($0.6 \text{ m}^2/\text{g}$ for electrolytic copper). As the molecular mass of the ultrafine fluoroplastic oligomer is $\sim 10\,000$ [20], about 10^{-3} g or 0.1 % of fluoroplastic can be accommodated on the surface of 1 g of copper. The sensitivity of thermogravimetric measurements is 10^{-2} – $10^{-4} \%$. (In Fig. 6, mass loss is normalized to the mass of fluoroplastic in the sample, and conversion was multiplied by -1 to maintain the conventional view of the derivatogram.)

If mechanical treatment of UPTFE with the components of the fusion mixture does not lead to structural changes, dispersion or interaction with the components, mass loss of the samples after treatment should develop in the same manner as for pure UPTFE.

Copper—UPTFE mechanocomposite

For mechanocomposite with copper, sublimation of fluoroplastic starts earlier and occurs stepwise compared to mechanically processed pure UPTFE and develops in steps (see Fig. 6, curve 2). This indicates that mechanical treatment with copper led to structure disordering, weakening the intermolecular bonds in fluoroplastic and (or) cleavage of the polymer chain, forming oligomers with smaller molecular masses.

The steps on the TG curve can be interpreted as the result of chemical interactions between the surface copper atoms and the dangling C—C or C—O bonds, forming stronger bonds to oligomers. A more detailed study showed that annealing of a pure copper sample mechanically activated under the same conditions occurs in a similar stepwise manner.

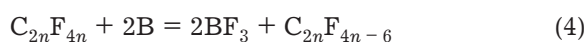
Complex research by various metal hardening methods [21] showed that the first step is due to the annealing of vacancies (most of these do not disappear on dislocations, but concentrate into clusters); the second is due to the disappearance of dislocations during recycling and recrystallization, and also to growth of grains during recrystallization. The nearly horizontal region between the peaks is related to dislocation redistribution and to continuous disappearance of vacancy clusters and packing defects. Therefore, UPTFE can be released from the copper matrix as a result of matrix restructurization. Additional experiments are necessary to establish whether the chemical bonds between copper and fluoroplastic undergo cleavage.

Titanium—UPTFE mechanocomposite

In this system (see Fig. 6, curve 3), the divergence of sublimation kinetics of UPTFE from that of the pure sample is greater. This may be evidence of bonding between titanium and fluoroplastic. The increased mass above 425 °C is probably due to impurities in the inert gas atmosphere used for sample heating and to the formation of titanium oxides along with sublimation.

Boron—UPTFE mechanocomposite

Sublimation of UPTFE already at 75 °C (see Fig. 6, curve 4) does not seem to be evidence of chain length shortening in fluoroplastic oligomer; rather, it is indicative of a chemical reaction that forms volatile boron fluorides in accordance with the following scheme:



This is supported by the fact that the observed mass loss exceeds the mass of fluoroplastic material in the mixture under investigation.

Thus preliminary mechanical treatment of the components of a fusion mixture with fluoroplastic probably changes the properties of the latter drastically. This partly explains its high qualities as a tribo-reagent. On the other hand, in some cases, mechanical activation accelerates chemical reactions *a priori* inconceivable in the system. Thus formation of boron fluorides that takes place on heating to several hundred degrees precedes SHS synthesis and hinders the formation of quality TiB₂ ceramics.

CONCLUSIONS

Solid-phase mechanochemical treatment gave new materials, namely, metal-fluoropolymer and metal-ceramics-fluoropolymer composites possessing high electric conductivity, low friction coefficient, and stability to mechanical abrasive action.

Using powder mixtures of immiscible metals (tungsten and copper) as an example, it has been demonstrated that addition of up to 1 % polytetrafluoroethylene during mechanochemical treatment affects the particle size of the resulting composite. In the presence of PTFE, composite particles 30–60 μm in size can be obtained; without an additive, large agglomerates several hundred microns in size are formed. The friction coefficient of W—Cu—UPTFE composite coating is close in magnitude to that of bulk fluoroplastic, which is of prime importance in manufacturing sliding electric contacts.

It has been demonstrated that thermal stability of PTFE that is part of mechanocomposites depends on the nature of the major component of the latter. Furthermore, it is controlled by bonding between PTFE and the component surface, by structural changes in components upon heating, and by potential chemical interactions, forming new products.

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