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Study of structure of copper-based composite materials during the spark plasma sintering

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Abstract. This paper is devoted to the study of copper-based composite materials structure formation processes in the conditions of SPS. The structures of Cu–Cr, Cu–Mo, Cu–W, Cu–Cr–Mo, Cu–Cr–W, Cu–Mo–W, Cu–Cr–SiC, and Cu–Zr–CNTs two-component and three-component systems were analyzed. The possibility of the formation of non-equilibrium phases under SPS conditions is shown, the effect of chemical transformations on the structure of bulk composite materials is considered.

1. Introduction

The spark plasma sintering (SPS) method has discovered new ways for producing materials with different properties due to the possibility of rapid and uniform heating combined with the application of pressure on the sample. For example, according to [1] from the 1960s, composite materials made of immiscible metals began to be used as contacts for vacuum interrupters. Conventional methods of powder metallurgy do not allow introducing something new into the structure and properties of such materials. The SPS method, due to the ability to preserve the nanostructure in the bulk material, again raised interest in contact materials, allowing one to create new composites with enhanced properties [2, 3]. However, the fundamental basis of the immiscible metals consolidation in the conditions of SPS is not yet fully understood.

2. Experimental

Commercial copper, chromium, tungsten, molybdenum, silicon carbide, carbon nanotubes, zirconium were used as initial materials. Composite powders were obtained in planetary ball mill "Activator 2S" (Activator, Novosibirsk, Russia). Pre-mixed powders were subjected to high-energy ball milling (HEBM) in an argon atmosphere in steel water-cooled vials containing 7 mm steel balls. The mass ratio of the balls to the powder was 20:1. The rotational speed of the sunwheel during process was 694 rpm with a vial-to-sunwheel rotation speed ratio (K coefficient) was equal to 1. Composite powders were consolidated in a spark plasma sintering device (SPS, Labox 650, SinterLand, Japan). The maximum load was 50 MPa.

The structure of the sintered materials was analyzed using a JSM7600F (JEOL, Japan) scanning electron microscopy (SEM). X-ray diffraction analysis was performed using a Diffractometer



(Scientific instruments, Russia). The density of the samples after sintering was evaluated using hydrostatic weighing. Electrical resistivity was measured at KRIOTEL (Russia) device using the four-contact method. The hardness of the sintered samples was determined on polished samples by the Vickers method according to GOST 2999-75 using a HVS-50 digital hardness tester.

The effect of the SPS parameters on the structure of materials obtained from composite particles of immiscible metals was studied. It was shown that during consolidation the structure of the particles changes: in binary systems (Cu–Cr, Cu–W, and Cu–Mo) heating leads to the growth of particles of refractory components from 5–10 to 200–300 nm with copper precipitation on the grain boundaries of sintered powders (figure 1).

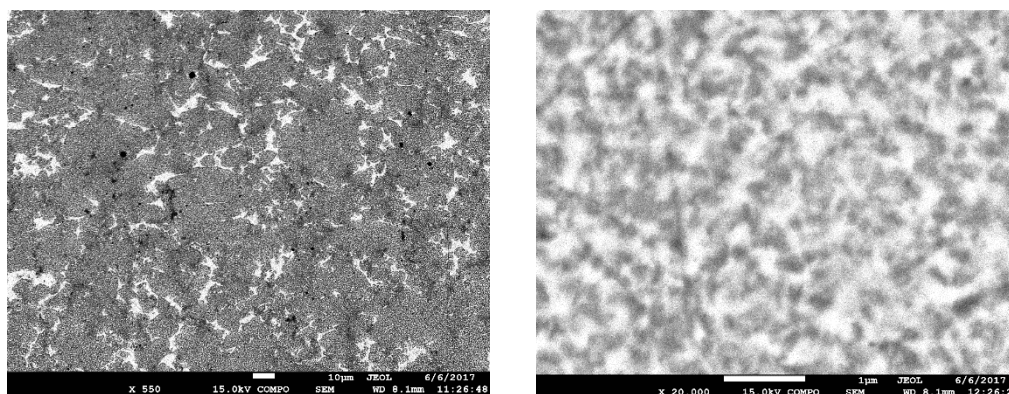


Figure 1. Cu–Cr structure after SPS at 700°C.

The structure of the Cu–Cr–W ternary composite also consists of homogeneous regions with inclusions between them. However, in some places small particles of tungsten are visible. The composition of homogeneous regions differs from the targeted, what can be explained by the copper precipitation along the boundaries, as well as the extrusion of plastic copper onto the sample surface due to overheating.

The structure of heterophase regions represents a matrix with tungsten and chromium inclusions. Cr and W powders disintegrated to the submicron sizes were overheating at the places of their contact during passing a current, forming a solid solution.

The structure of Cu–Mo–W samples also represents a heterophase region separated by a copper phase. However, in contrast to the Cu–Cr–W sample, the heterophase regions are uniform; they do not contain large inclusions of individual components. These areas consist of solid solution particles of refractory components in a copper matrix.

The microstructure of the Cu–Cr–Mo sample is completely similar and comprises heterophase region of a solid Cr–Mo solution in a copper matrix surrounded by copper inclusions formed during sintering.

The 50Cu–25Cr–25SiC and 50Cu–40Cr–10SiC materials were also investigated (the numbers indicate the volume percentage of the components).

In contrast to previous systems, the nanocomposite structure was destroyed in samples containing silicon carbide (figure 2). However, it is worth noting the presence of several phases in the back scattered electrons. The performed X-ray analysis showed a change in the phase composition relatively to the powder material, and this change is different for different SiC contents.

Thermodynamic analysis of the Cu–Cr–SiC system with a given compositions at the sintering temperature showed that in the presence of 10 vol % SiC in the initial mixture, the equilibrium composition of the solid phase will be Cu–Cr–Cr₃Si–Cr₂₃C₆. For the system initially containing 25 vol % SiC, the composition of the solid phase will be Cu–SiC–Cr₅Si₃–Cr₃C₂. Unfortunately, due to the similarity of the structures, the quantitative analysis of the phase composition is difficult, but it can be concluded that the reactions do not reach equilibrium under sintering conditions (heating to 900 °C at a rate of 100°/min and holding for 15 min). This is evidenced by the peaks of the intermediate phases Cr₇C₃ for the composition 50/40/10 and Cr₃Si for the composition 50/25/25.

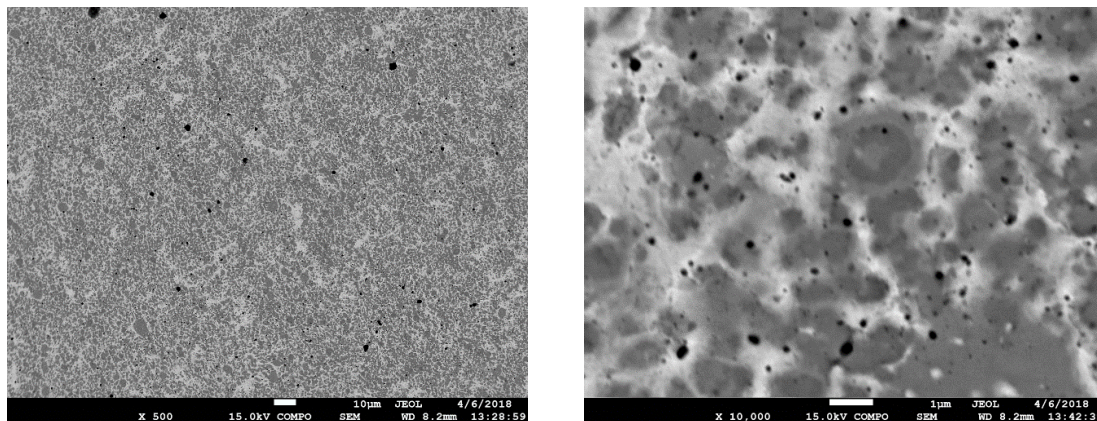


Figure 2. Microstructure of the Cu–Cr–SiC with the 10 vol % SiC.

Thus, the interaction of chromium with silicon carbide leads to the destruction of the nanocomposite structure of the powders during consolidation. The causes of this phenomenon could be the diffusion effects due to composition change, as well as a sharp increase in electrical resistance (change in the lattice type, the appearance of microstresses and other defects), leading to local overheating in the structure and accelerating mass transfer processes.

The study of the Cu–Cr–CNT sample using a scanning electron microscope showed that the structure of the material represents heterophase regions of various sizes, separated by copper inclusions, as in above-mentioned cases of binary and ternary metal systems. Energy dispersive analysis showed that heterophase regions consists of chromium, copper and carbon. However, X-ray diffraction analysis showed only two phases in the sample composition: copper and chromium carbide (II). As a result, we can conclude that long-term high-energy ball milling leads to the destruction of CNT and the intensification of the interaction processes between carbon and chromium.

Similar results were obtained for the Cu–Zr–CNT system. Powders for sintering with 50 at % Cu, 12.5 at % Zr, and 37.5 at % C were prepared in two ways: mixing in the roller mill and in the planetary ball mill.

The structure of the sample after consolidation of the roller milled powders represents copper and zirconium grains separated by the CNT agglomerates (figure 3). Zirconium concentration in the grains is not uniform; it mainly located at the edges of particles (figure 3b, 3c). X-ray diffraction analysis of the roller milled powders before and after sintering shows that a small peak of zirconium carbide appears in the structure of the sample, i.e. sintering conditions contribute to the formation of a compound between the components, but at a low rate.

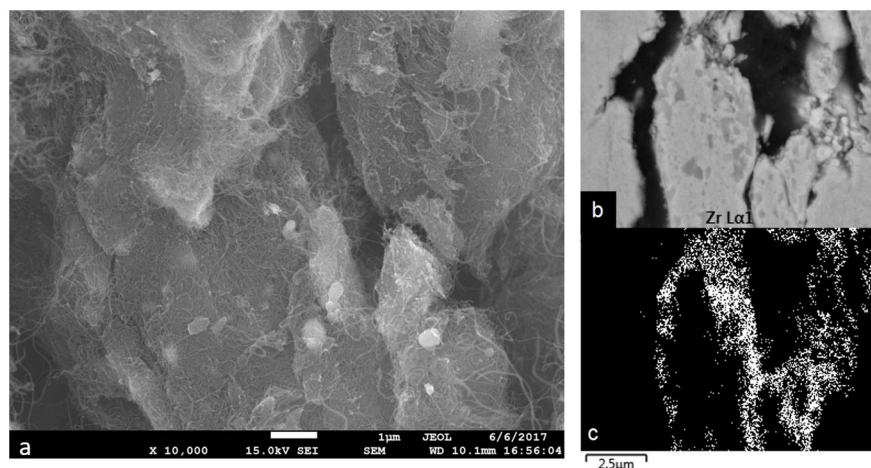


Figure 3. Microstructure of Cu–Zr–CNT powder after mixing in the roller mill.

Structure of the fractured sample obtained by the HEBM + SPS method differ from the sample after roller mill. The morphology of the initial particles is clearly visible on the surface of the fracture: there are rather large areas, to which small areas have been sintered. However, chemical interaction between zirconium and carbon occurred leading to the formation of the carbide phase.

3. Conclusion

By combining the HEBM and SPS methods, it is possible to obtain a structure consisting of heterophase regions of submicron (up to 300 nm) particles of refractory materials uniformly distributed in a copper matrix. Adding a third component does not lead to significant changes in the microstructure of the material, if the refractory components form a solid solution. Chemical transformations, on the contrary, lead to significant changes in the microstructure: to an increase in the size of the structural components and the formation of non-equilibrium phases.

Acknowledgments

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