JOURNAL OF MATERIALS SCIENCE **40** (2005) 3491 – 3495

Nanocomposites TiB_2-Cu: Consolidation and erosion behavior

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In this work we report consolidation and erosion behavior of TiB_2-Cu nanocomposites showing increased stability during electric erosion in high-current arc discharge. Composite powders containing nanoparticles of titanium diboride distributed in copper matrix were synthesized using high-energy ball milling and then shock wave consolidated to obtain fully dense compact electrode material with retention of the size of particulate inclusions. Copper weight losses by evaporation in composite electrodes were 10 times lower compared to pure copper electrodes and arc spot size was about an order of magnitude increased indicating distribution of arc on a larger surface. Porous Cu-depleted layer was formed on the surface of composite electrode and no copper melt was observed to squeeze out on the surface so that the electrode held its shape and size. The improved erosion resistance of the electrode material is believed to be due to its nanocomposite structure. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Rapid development of devices employing high-current arc discharges stimulates research on erosion-resistant materials. High conductivities are essential advantages of metallic copper; however, when resistance to electric erosion at high current is concerned, pure copper is extremely unstable resulting in rapid degradation of the electrode due to evaporation and flow of molten drops from the surface. The problem of electric erosion is of primary concern in high current breakdown switches and rails of electromagnetic launches. The trend in the development of electrode materials for high-current applications is the design of copper composites containing high melting components (metals or ceramics). Cu-W, Cu-Mo and Cu-Al_2O_3 composites have already shown promise as materials with increased resistance to electric erosion compared to pure copper [1]. Required stability to erosion of these composites is provided by the presence of rigid W or Mo skeleton. Improved erosion resistance of Al_2O_3-Cu composites is achieved when the volume content of alumina particles is less than 20% [2, 3]; however, the mechanism of increasing stability is not well understood.

Conventional electrodes made of monolithic copper are "passive" to the processes of formation and operation of arc discharge. When composite materials are used, there appear possibilities of controlling erosion processes. It is considered [4] that centers of intensive electron emission are localized on particulate inclusions, grain and interfacial boundaries. During formation of arc discharge with high current density microspots are grouped on the surface defects. Degradation of the electrode can be significantly reduced if arc spot is enlarged resulting in reduced roughness of the eroded surface.

Composite materials with nanograined or nanodispersed structure satisfy these requirements. In this consideration we investigated erosion behavior of TiB_2-Cu nanocomposite electrodes. A wide interest to TiB_2-Cu system is manifested by a large number of recent publications [5–8] and is due to successful combination of conductive ductile metal and conductive ceramic with high melting point and hardness.

Thus, we present preparation of bulk TiB_2-Cu nanocomposites and discuss erosion behavior of nanocomposite electrodes.

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2. Experimental

2.1. Preparation and consolidation of TiB_2-Cu nanocomposites

Synthesis of TiB_2-Cu nanocomposites was described elsewhere in detail [9]. Nevertheless, it is important to note that processing included mechanical treatment in high-energy planetary ball mill (AGO-2, Model of Institute of Solid State Chemistry and Mechanochemistry SB RAS, Russia). High-energy treatment (acceleration of balls was 600 $m \cdot s^{-2}$) allowed obtaining high concentrations of defects in powders treated.

Ti-B-Cu elemental powders were milled and then ignited to initiate self-propagating reaction to form titanium diboride. The product of SHS reaction was then mechanically treated to decrease the size of titanium diboride particles.

As the matrix content in the product of SHS-reaction is limited the advantage of this three-stage processing is the possibility of introduction additional quantity of metal powders during mechanical treatment of the SHS-product. In this work we produced SHS-product with 57 vol% of titanium diboride and then diluted it by copper to obtain 18 vol%TiB_2-Cu composition. The size of TiB_2 particles distributed in copper matrix in the resultant product was 30–50 nm [9–11]. The average size of composite powder particles (agglomerates) was 30–40 μm.

Shock wave compaction was employed for production of electrodes. Experimental details of shock wave compaction are described in [12].

2.2. Erosion tests

Erosion tests under conditions of high current arc discharge were performed using the model of coaxial accelerator [2] (Fig. 1). Time of the discharge was 50 μs and the maximum current was 180 kA. Erosion rate was measured by weight losses of the electrode.

2.3. Microstructure studies

Microstructures of as-compacted samples and electrodes after erosion tests were investigated using Scanning Electron Microscopy (SEM) and Optical Microscopy. To prepare samples for SEM the compacts were polished and etched with $FeCl_3$-H_2O-ethyl alcohol or $(NH_4)_2S_2O_8$ aqueous solution.

3. Results and discussion

The volume content of the refractory component in electrode materials must correspond to the required conductivity level, mechanical properties and erosion resistance. Taking into account the results of [2, 3] showing improved erosion resistance of Al_2O_3-Cu composites containing alumina particles less than 20 vol%, we have chosen 18 vol%TiB_2-Cu composition for this study.

According to considerations presented above, consolidation of nanocomposite powders must be performed with retention of the inclusion particle size. Consequently, the methods of consolidation that exclude particle growth and give high densification will be suitable. This is successfully realized in shock wave consolidation due to highly non-equilibrium conditions of the process and high-pressures involved. In addition, the required cylindrical shape of the electrode can be also easily constructed choosing the shape of consolidation ampoule. As the erosion stability is mainly determined by the structure of the subsurface layer of the electrode, the surface layer was made of the nanocomposite material while the internal part was made of pure copper (copper stem). The total diameter of the electrode is 6 mm.

Fig. 2a shows the microstructure of TiB_2-Cu powders in transmission electron microscope. Titanium diboride particles 30–50 nm in size are uniformly distributed in copper matrix. These nanocomposite powders were

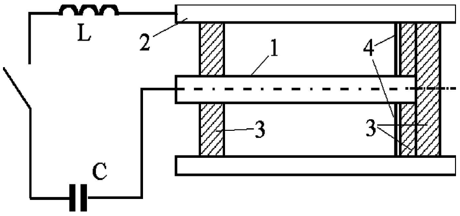
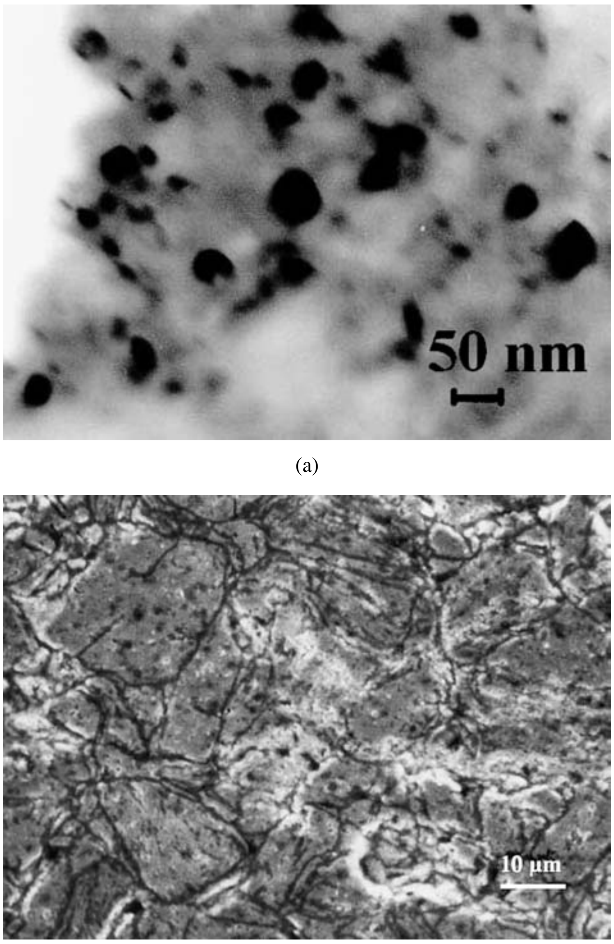


Figure 1 Scheme of the set-up for arc discharge erosion tests (model of coaxial accelerator): 1-electrode, 2-cylindrical electrode, 3-insulator, 4-copper foil.



(a)

(b)

Figure 2 Microstructure of TiB_2-Cu nanocomposite: a—nanocomposite powders (Transmission Electron Microscopy image); b—microstructure of shock wave compacted 18 vol%TiB_2-Cu nanocomposite (SEM image).

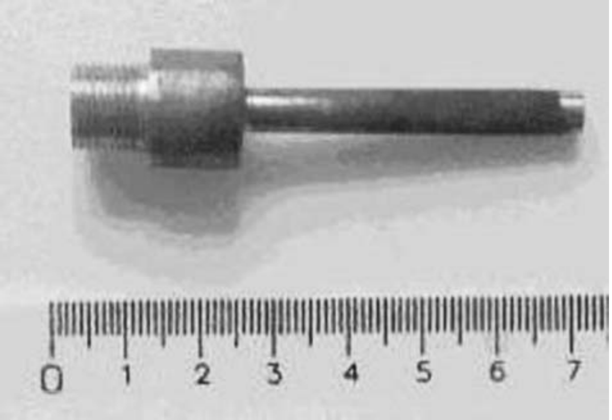


Figure 3 General view of TiB_2-Cu electrode (the surface is eroded after the erosion test).

compacted using shock wave consolidation in a steel ampoule. The features of the compaction under shock wave conditions include the absence of liquid phases and extremely high pressures (about 3 GPa). The process of compaction is very rapid. Due to these factors the growth of titanium diboride particles does not take place during the compaction. The microstructure of 18 vol%TiB_2-Cu shock wave compacted electrode (Fig. 2b) is uniform and composed of powder particles (agglomerates) closely packed to each other. $FeCl_3$-H_2O-ethyl alcohol mixture and $(NH_4)_2S_2O_8$ aqueous solution used for etching selectively remove copper from the surface so that titanium diboride particles can be distinguished. However, no enlarged particles of titanium diboride were revealed through etching of the polished surface. This indicates the absence of particles growth during shock wave consolidation of nanocomposite powders. The compact has high density (more than 98%) and is suitable for making the parts by machining.

General view of shock wave compacted electrodes after electric erosion is shown in Fig. 3. The weight losses of the nanocomposite electrode of the described configuration during erosion tests were 3 mg, while those for pure copper electrodes are about 30 mg under the same conditions. Chemical analysis showed that the substance removed during erosion from the surface of the electrodes is copper containing only traces of titanium. These results were reproducible and allowed us to conclude that erosion resistance of nanocomposite 18 vol%TiB_2-Cu electrodes is 10 times improved compared to electrodes of the same diameter and length made of monolithic copper.

Due to copper evaporation pores 20–30 μm in size were observed on the surface of the nanocomposite electrode (Fig. 4) and porous subsurface Cu-depleted layer 30–50 μm thick was formed that can be seen in the cross-section of the electrode (Fig. 5). No copper melt was observed to squeeze out on the surface of the electrode (Fig. 6a) so that the geometrical parameters of the electrode (shape and size) were retained. This situation is quite unusual, for in conventional Cu or microcomposite Mo-Cu, W-Cu and Al_2O_3-Cu electrode materials pools of refrozen copper are always observed on the surface indicating that the melt was partially squeezed out on the surface (Fig. 6b).

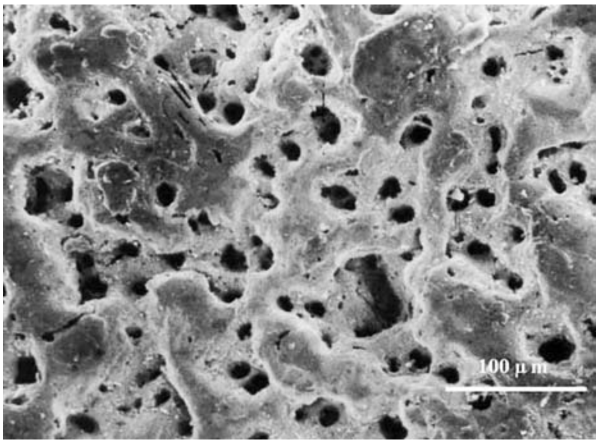


Figure 4 Microstructure of the surface of 18 vol%TiB_2-Cu nanocomposite electrode after electric erosion (SEM image).

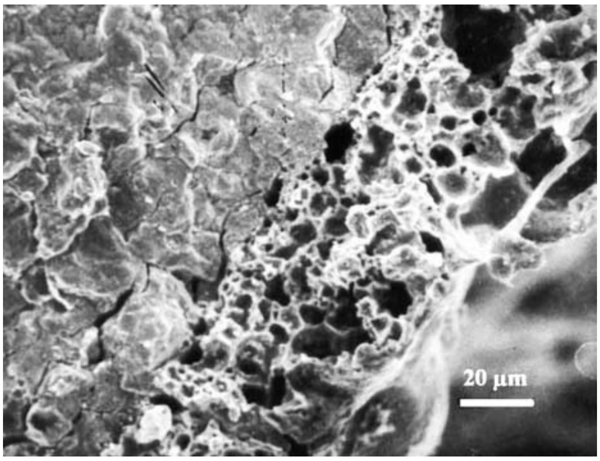
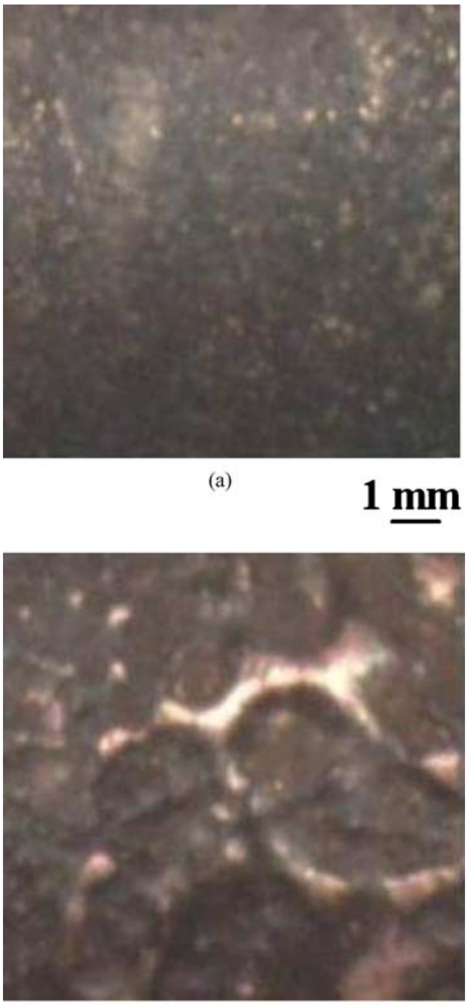


Figure 5 Porous Cu-depleted layer formed on the surface of 18 vol%TiB_2-Cu nanocomposite electrode during electric erosion (SEM image of the crosssection of the electrode).

The roughness of the eroded surface of 18 vol%TiB_2-Cu nanocomposite electrode is quite uniform. The length of the eroded area is about 3 cm (Fig. 3) that is about 10 times larger compared to Cu or W-Cu electrodes of the same geometrical configuration. In Cu and W-Cu electrodes the area damaged by erosion is about 2–3 mm long. The typical structure of this area is shown in Fig. 6b. So, the arc spot size was an order of magnitude increased compared to that for pure copper electrodes. The composite structure of the surface and the presence of nanoparticulate inclusions could facilitate formation of numerous microspots. So, nanocomposite electrodes were "active" in arc formation.

The decrease in weight losses of the electrode can be also achieved by design of metal-metal composites such as Mo-Cu, W-Cu and Al_2O_3-Cu reported in [1–3]. In [2, 3] Mo-Cu, W-Cu and Al_2O_3-Cu microcomposites (composies containing micron particles) were shock wave consolidated and tested at the same conditions. The degree of erosion stability greatly depends on the composition of these materials. For W-Cu and Mo-Cu composites erosion stability is better than that of pure copper when copper volume content is between 30–70%. As was mentioned above, improved erosion resistance of Al_2O_3-Cu composites is achieved when



(a)

(b)

Figure 6 Surface of the electrodes after electric erosion (optical images): a—18 vol%TiB_2-Cu nanocomposite electrode, b—W-Cu electrode compacted from powders of micron size.

the volume content of alumina particles is less than 20%. When optimal composition is provided, W-Cu, Mo-Cu and Al_2O_3-Cu composites can be 5–10 times more stable than pure copper, and, consequently, their erosion resistance is comparable with that of nanocomposite TiB_2-Cu material developed and studied in this work. However, the mechanism of erosion in Mo-Cu, W-Cu and Al_2O_3-Cu composites, i.e. the process in the materials that take place during the discharge, is very similar to that of pure monolithic copper. Copper melt comes out from the eroding layer to the surface of the electrode so that formation of copper pools and flow of molten droplets with the vapour phase are unavoidable. Refrozen melt forms thumbs on the surface of the electrodes (Fig. 6b) that behave as concentrators of arc resulting in rapid damage of these areas and destruction of the electrode under subsequent working cycles. This problem is solved in nanocomposite TiB_2-Cu material.

So, when passing from composites containing inclusions or grains of micron size to nanostructured material the mechanism of electrode degradation changes from the one based on copper melting and flow of molten droplets to that related to copper evaporation. Formation of porous TiB_2-enriched layer during erosion and the absence of copper thumbs on the surface of TiB_2-Cu nanocomposite electrodes indicates a new erosion mechanism that gives not only resistance to electric erosion during the first erosion test but improved erosion behavior of the material during the subsequent performance as well.

Conventional methods of conserving the shape and size of the electrodes thus increasing its service life are making a refractory skeleton within a material. In this case porous preform is usually infiltrated with molten metal [13]. To achieve the required connectivity between ceramic particles they are firstly covered by polymer binder. It is rather a task to ensure complete burning-out of the binder under increasing temperature; therefore, evolution of carbon oxides during the performance of the electrode can cause its additional degradation. For the same reasons the use of electrodes containing carbide inclusions is rather limited. Unreacted carbon that can be remained due to incompleteness of the reaction with the carbide-forming metal oxidizes at high temperatures. The gaseous products form bubbles, which evolve from the molten metal. As a result, flow of melt droplets from the surface of the electrode may be observed. Degradation of the electrode drastically increases in this case.

So, the great advantage of the composites electrodes consolidated from powders containing nanoparticulate boride inclusions formed in situ in the matrix is the absence carbon substances in all stages of processing. Moreover, formation of the refractory skeleton, which causes a problem for machining operations and increases the tendency of metal-ceramic material to spalling and formation of microcracks, appears to be unnecessary when we deal with nanocomposite electrodes described in this study. The shape and the size of the nanocomposite electrodes are well enough conserved.

4. Summary

TiB_2-Cu nanocomposite powders containing titanium diboride particles 30–50 nm in size distributed in copper matrix were successfully consolidated by shock wave. Due to short time impact and high-pressures involved full densification was achieved during compaction and the growth of titanium diboride particles was inhibited.

Potential of bulk TiB_2-Cu nanocomposite as a promising material with improved resistance to electric erosion in high-current arc discharge was evaluated. Nanocomposite electrodes showed 10-fold increase in erosion stability measured by weight losses compared to pure copper electrodes. The mechanism of degradation of the nanocomposite electrodes changed compared to that for copper or tungsten-copper electrodes with micron grains. The presence of nanoparticulate inclusions and high content of grain and interfacial boundaries favored formation of numerous arc microspots resulting in about an order of magnitude increase in arc spot size. No copper was squeezed out but porous TiB_2-enriched layer was formed on the surface of the electrode so that it retained geometrical parameters and showed increased service life. New materials can be developed on the basis of this system, for example, composites containing tungsten and titanium diboride dispersed copper. In such materials two mechanisms of improvement erosion stability can be combined.

Acknowledgements

This work was supported by Research Center for Machine Parts and Materials Processing (ReMM) at University of Ulsan, Korea.

References

1. W. R. WILSON, *Trans. AIEE* **74** (1955) 657.
2. G. A. SHVETSOV, V. I. MALI and A. G. ANISIMOV, in Proceedings of the 6th European Symposium on EML Technology (Netherlands, 1997) p. 117.
3. *Idem.*, *IEEE Trans. Magn.* **33** (1997) 410.
4. A. D. LEBEDEV and K. V. MALEVINSKY, in Proceedings of I Seminar on Dynamics of High-Current arc Discharge in Magnetic Field (Novosibirsk, Russian, 1990) p. 160.
5. S. J. DONG, Y. ZHOU, Y. W. SHI and B. H. CHANG, *Metall. Mater. Trans. A* **33A** (2002) 1275.
6. C. BISELLI, D. G. MORRIS and N. RANDALL, *Scripta Metall. Mater.* **30** (1994) 1327.
7. J. P. TU, N. Y. WANG, Y. Z. YANG, W. X. QI, F. LIU, X. B. ZHANG, H. M. LU and M. S. LIU, *Mater. Lett.* **52** (2002) 448.
8. S. C. TJONG and Z. Y. MA, *Mater. Sci. Eng.* **29** (2000) 49.
9. Y. S. KWON, D. V. DUDINA, M. A. KORCHAGIN, O. I. LOMOVSKY and H.-S. KIM, *J. Metast. Nanocryst. Mater.* **15/16** (2003) 253.
10. N. Z. LYAKHOV, V. E. PANIN, D. V. DUDINA, M. A. KORCHAGIN, O. I. LOMOVSKY, YU. V. GRINYAEV, V. G. DURAKOV, S. V. PANIN and YU. I. POCHIVALOV, *Phys. Mesomech.* **6** (2003) 63 (in Russian).
11. Y.-S. KWON, D. V. DUDINA, M. A. KORCHAGIN and O. I. LOMOVSKY, *J. Mater. Sci.* **39** (2004) 5325.
12. V. I. MALI and T. S. TESLENKO, *Combustion, Explosion and Shock Waves* **38** (2002) 473.
13. S. NORASETTEKUL, P. T. EUBANK, W. L. BRADLEY and B. BOZKURT, *J. Mater. Sci.* **34** (1999) 1261.

Received 1 September 2004
and accepted 12 January 2005