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Preparation of nano-Al_2O_3 dispersion strengthened coating via coating-substrate co-sintering and underwater shock wave compaction

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Abstract

This paper aims at developing a process technology to fabricate an aluminum dispersion strengthened coating on a copper substrate. First, nanostructured Cu–Al_2O_3 powder was prepared by hydrogen-reduction of mechanical alloyed Cu and Al_2O_3 mixed powders. Low-density coating was then achieved through die pressing and pre-co sintering. Finally, dynamic consolidation by underwater shock wave was used to densify the Cu–Al_2O_3 sintering body, ensuring strong bonding between the coating and substrate. The compressing process was simulated using the commercially available package LS-DYNA. Numerical simulation gave deformation of the coating layer and pressure distribution during the compressing process. Microstructure characteristics indicate that the coating layer has a uniform and fine-grained composite structure and a strong surface bonding between coating layer and copper substrate. The fracture surface, analyzed by SEM, showed intergranular fracturing. Measurement of hardness showed a high hardness value, indicating sound mechanical properties of the coating layer. This method has thus been proven feasible for preparation of aluminum dispersion strengthened coating on copper substrate.

Keywords: Aluminum dispersion strengthened coating; Nano-Al_2O_3; Coating-substrate co-sintering; Underwater explosive compaction

1. Introduction

Oxide dispersion strengthened (ODS) copper alloys have been suggested for such applications as high-performance switches, heat exchangers, and contact materials [1,2] due to their high thermal conductivity and high strength; such applications often apply to materials thermal shock, surface erosion and high heat load. However, fabrication of large volume ODS copper alloys currently entails high cost and technique difficulties. This paper advances a preparation method to fabricate dispersion strengthened coating onto pure copper surface allowing the dispersion strengthened coating to directly face the burdens of thermal shock, surface erosion and heat load. The copper substrate acts as a heat-sink material to transfer the heat loads from the coating to the water coolant.

Alumina particles (Al_2O_3) have been adopted as the ODS material due to their superior advantages such as high hardness, high melting point, excellent thermal stability and chemical inertness. Also, Al_2O_3 particles are insoluble in copper matrix and have the ability to retain their original shape, size, spacing and distribution even after prolonged exposure to elevated temperature. Therefore, dispersion distributed Al_2O_3 particles can increase recrystallization temperatures and exhibit excellent strength at elevated temperatures by constricting grain and sub-grain boundaries of the copper matrix and impeding the movement of dislocations. Furthermore, aluminum dispersion strengthened (ADS) copper has almost the same electrical and thermal conductivities as pure copper but better creep and arc erosion resistance at elevated temperatures.

The preparation technology includes following processes: mechanical alloying, die pressing, hydrogen pre-sintering, and underwater explosive compaction. Mechanical alloying (MA), or ball-milling of mixed powers and a subsequent

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hydrogen reduction, has been suggested as a method to prepare Cu–Al_2O_3 nanocomposite powders. Homogeneous Cu–Al_2O_3 nanocomposite powders as source materials show an improved sinterablity due to decreased particle size and enhanced rearrangement of Al_2O_3 particles [3–5]. Pre-sintering at 900 °C reduces heterogeneity of different materials and ensures the coating layers adhere to the substrate, and the fine coating-substrate co-sintering process potentially generates a strong bonding between the alumina dispersion strengthened coating and the copper substrate. Underwater explosive compaction utilizes underwater shock waves generated by underwater detonation of an explosive to provide extremely high pressure (1–20 GPa) within several microseconds. The duration of the loading pressure is so instantaneous that the crystal grains have no time to increase in size, while particles impact at a time scale so fast as to produce minimal surface heating and a high quench rate. Consequently, nanostructure during consolidation was maintained.

In this paper, we attempt to fabricate alumina-dispersion-strengthened coatingonto copper substrate. Commercially available package LS-DYNA was used to stimulate the compressing process. The aim of the present work is to analyze the mechanism of this new preparation method and to evaluate the quality of the composite plate through studying the microstructure, micro-hardness and fractography of the composite. Processing issues and problems encountered during experimental trails will be discussed; however, the paper is primarily focused on the processing of the coating-substrate material as many processing details require further study.

2. Theoretical analysis

Fig. 1 shows a schematic illustration of the coating process.

The high energy milling the Cu–Al_2O_3 mixing powders in the first step promotes mechanical alloying, which causes severe mechanical plastic deformation of the powders due to ball-to-ball and ball-to-wall collisions, significantly enhancing the generation of dislocation. Powder fracturing during MA introduces defects into powder and generates new clean surfaces that are beneficial for atomic diffusion. MA continuously mixes, cold-welds and fractures the powder mixture. The final product after milling generally consists of agglomerated powders that can be either solid solution or a mixture of phases of micron or nanometer sizes of crystalline or amorphous nature [6]. After MA, the Al_2O_3 particles are embedded within the copper particle matrix.

In step 2, the milled, hydrogen-reduced Cu–Al_2O_3 powders are pre-compacted to the surface of copper. The Cu–Al2O3 powder mixture following pre-compacting has a 60–70% theoretical densities (TD), and particles stick to the copper substrate, which is beneficial for the following steps.

Step 3 has the pre-compacted mixed-coating substrate heated to a temperature below the melting point to create a solid state. During this sintering, the mixed powders undergo four processes: contact point particles bond; contact points grow into necks; pores reduce in size; and grain boundaries develop in place of the necked regions. The sintering process is useful in promoting interparticle diffusion. In this case, the Cu particles build into a network because they are ductile particles that exert an important effect on the densification of the composite. Breaking up the agglomerates of MA powder is difficult following cold compaction as that process generally leaves residual porosity, small cracks and voids even after sintering.

Thus, step 4 utilizes underwater explosive compaction, a very rapid and intense deposition of shock energy to the

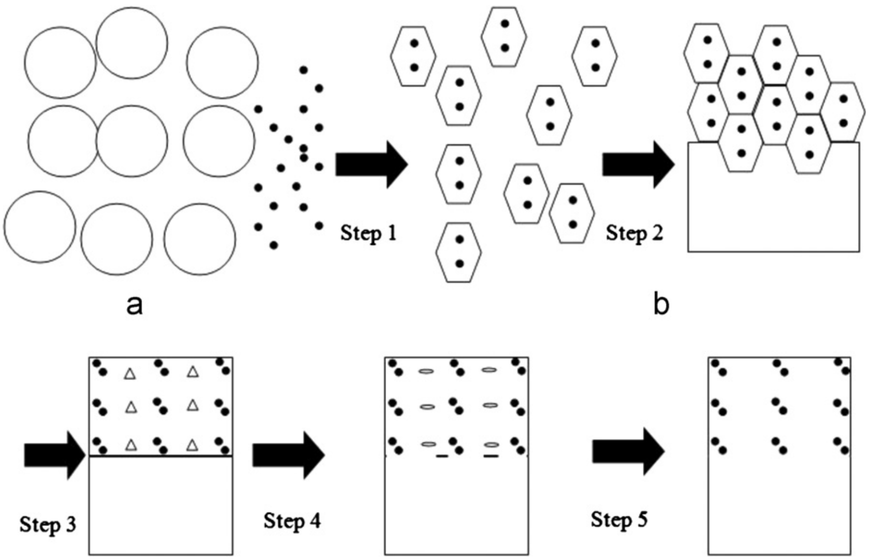

Fig. 1. Schematically illustration of the coating process.

powder particle surfaces, to produce consolidation [7–9]. During pressurization and acceleration by the underwater shock wave generated by the detonation of an explosive, an intensive deformation of the powder surface is induced which causes the powder surfaces to undergo melting and solidification in microseconds. Residual porosity, small cracks and voids generated in the sintered body will disappear under the action the underwater shock wave.

In step 5, the specimen undergoes vacuum sintering again. During the sintering process, residual stress caused by underwater shock waves is eliminated, allowing closure cracks and voids to bond together.

Through the five steps, a fully densified alumina dispersion strengthened coating on copper substrate may be obtained.

3. Experiment procedure

3.1. Mechanical alloy

Raw materials used in this study were electrolytic copper powder with particle size of about 74 μm and Al_2O_3 powder with particle size of about 100 nm; their mass ratio was 98:2. The two selected compositions of Cu–2%Al_2O_3 were high-energetically ball-milled at a milling speed of 400 rpm for 24 h in a QM-BP planetary ball mill. The mass ratio for the steel balls and mixed powder was about 7:1. During ball milling, the very hard Al_2O_3 particles embed in the soft Cu particles such that the Al_2O_3 particles gradually dispersed, while the Cu particles deformed, fractured and cold welded repeatedly. The milled powder mixture was heated to a temperature in hydrogen atmosphere of about 300 °C for 30 min to eliminate oxygen in copper. Because oxygen can combine with copper to form CuO, which will immensely reduce density, strength and electric conductivity of Cu–Al_2O_3 bulk material.

3.2. Hydrogen sintering

The Cu–Al_2O_3 powder mixtures were pre-compacted to the copper (pure) substrate by uniaxial pressing (UP) to a relative density of 60% theoretical density. The pre-compacted mixed-powder coating and the copper substrate were co-sintered at 300 °C, 600 °C and 850 °C for 30 min, 30 min and 60 min, respectively, in a hydrogen atmosphere with a heating rate of 10 °C/min. Sufficient sintering of the mixed powder ensured full diffusion of interparticles and densification of pre-compacted powder mixtures.

3.3. Underwater explosive compaction

Fig. 2 shows a schematic illustration of underwater explosive compaction. The device typically consists of several parts, including a water container, electrical detonator, explosive container and pre-compacted powder coating with copper substrate. A special mixed explosive (ANFO), whose detonation velocity is set at 3000 m/s and is commonly used for explosive welding, was adopted for underwater explosive compaction. The explosive density was 1 g/cm^3, and the explosive thickness was 30 mm. The ADS coating layer and copper substrate were sealed against water. All these parts were submerged into water. By triggering the electric detonator, the shock wave propagated in water directly acted on the mixed powders, which induced consolidation and high bonding strength between the ADS coating and copper substrate. Finally, the compacted ADS coating and copper substrate were co-sintered at 800 °C for 1 h to eliminate microcracks and micropores so as to improve the coating quality and bonding strength.

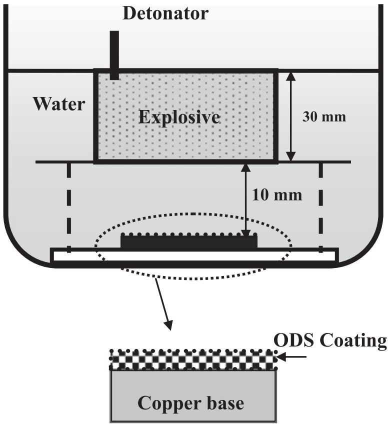

Fig. 2. Experimental set-up employed for underwater explosive compacting.

4. Numerical analysis

Computer modeling of the underwater compaction process, including explosive detonation, propagation of shock wave in water, and compaction of the coating layer was developed using LS-DYNA. The pressure of the detonation products was calculated using the JWL (Jones–Wilkins–Lee) equation of state. The pressure of the water was obtained using the Grüneisen equation of state. The coating layer and the substrate were treated as Johnson and Cook type plastic material, and the Grüneisen equation of state was used to calculate the pressure on them. As showed in Fig. 3, the explosive, water and substrate were divided into sub-grids made up of rectangular cells, with the size of each element 0.05×0.05 cm, apart from the element for the coating layer, which was 0.02×0.02 cm. The contact used in the program was automatic surface to surface contact. Parameters such as pressure, velocity, stresses and strains, and displacement were calculated for each cell.

Fig. 4 shows the deformation processes of the coating layers under the action of underwater shock wave. The reflected wave can be seen at the point at which shock front arrived on the coating layer. The coating layer was compressed by pressure shock. Then an oblique shock wave was generated inside the coating layers. At the same time, oblique shock wave propagated to the substrate and ensured a strong bonding between the coating layer and substrate, and as a result the pressure distribution appeared as two peaks. The mixed-powder coating was compressed from left to right, and thickness was attenuate.

The pressure inside the coating layers for different horizontal positions of x 1–5 cm is given in Fig. 5. Equal pressure ensured the coating layers were compressed uniformly and that the Al_2O_3 powder was well distributed inside the coating.

Numerical analysis gave a rough proximation of propagation of shock wave in water and coating and of the compression process, which provided direct guidance for experiments.

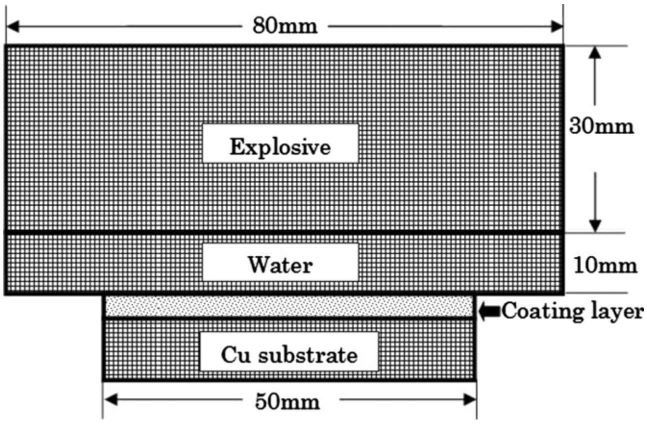

Fig. 3. The numerical model of the underwater explosive compaction.

5. Results and discussion

Visual and light optical inspection of the face reveals a structure without visible cracks, pores, or separation of the coating layer and substrate. Fig. 6 shows a cross-section image of the coating zone. The coating layer has a uniform and fine-grained composite structure. Fig. 6 confirms that the milled powders were completely consolidated, with no cracks observable. It can be seen that there are bright areas and relatively dark areas, representing different Al_2O_3 content: The bright areas indicate relative lower Al_2O_3 content with particle size of 5–20 μm in the middle parts of the alloy particles; the dark areas indicate relative high Al_2O_3 content, which are in the original surface layers of alloy particles [10]. It can be concluded that the sintering and underwater shock compaction did not coarsen the fine-milled powder but helped to maintain their original fine size, mainly due to the confining effect of Al_2O_3 particles on the movement of the alloy particles.

Fig. 7 shows SEM image near the interface of the joint. As can be seen, there was no separation at the interface zone, and the coating layer and the copper substrate bonded together well. After sintering and underwater shock wave compaction, the particles near the interface from both coating layer and copper base diffused-bonded. Integrated interface predicts high bonding strength.

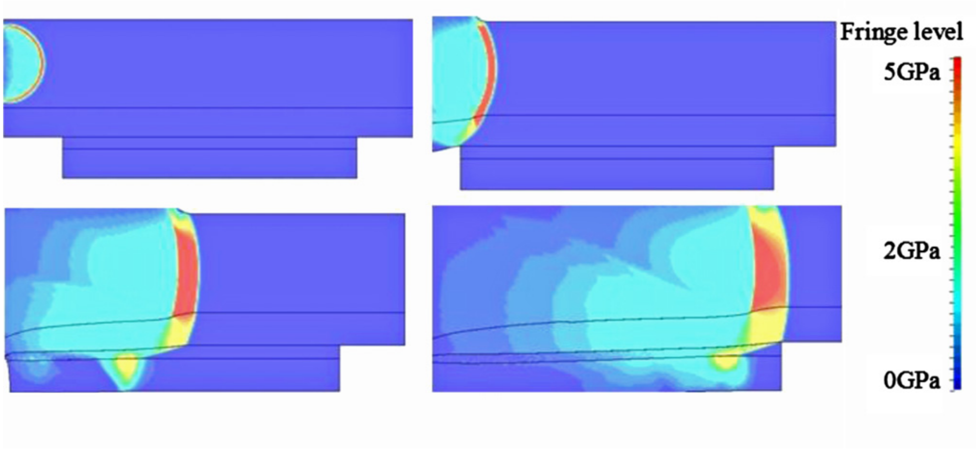

Fig. 4. Deformation process of coating layer and pressure distributions during the compressing process.

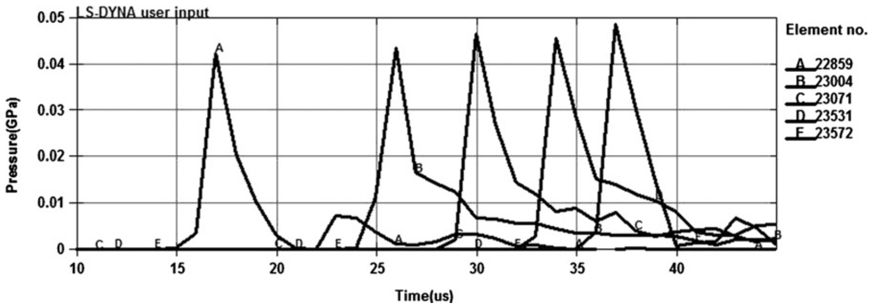

Fig. 5. Pressure distribution of inside the coating layer at various horizontal positions.

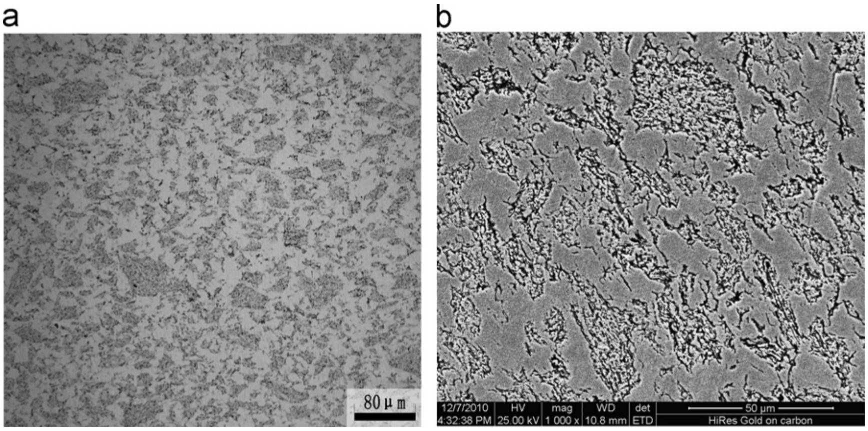

Fig. 6. Microstructure of the cross-section of the Cu–Al_2O_3 composite, (a) Optical images, (b) SEM image.

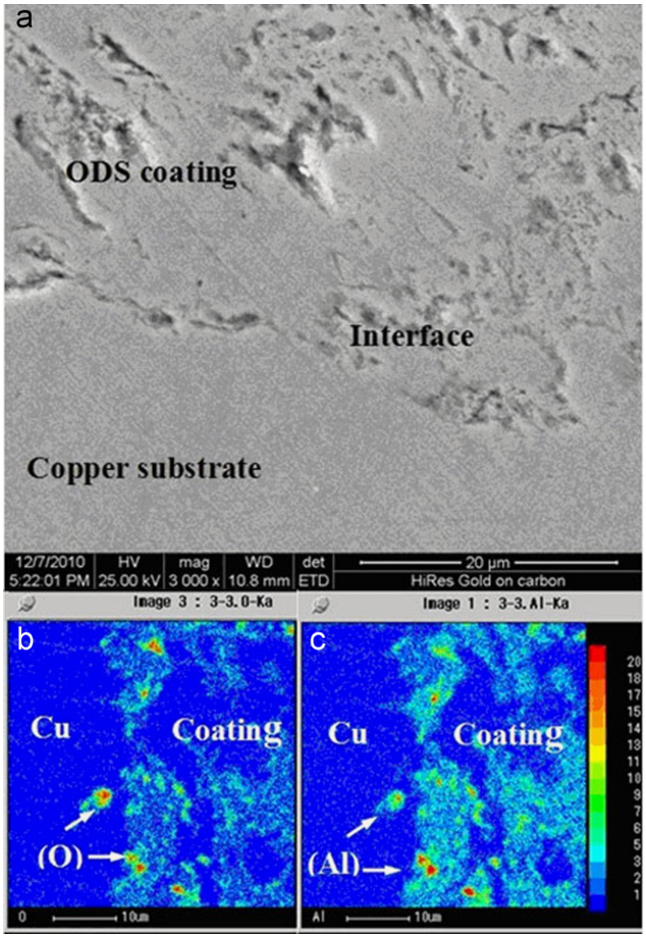

Fig. 7. (a) Microstructure of the interface zone; Elemental mappings of the interface using EDS (b) O mapping, (c) Al mapping.

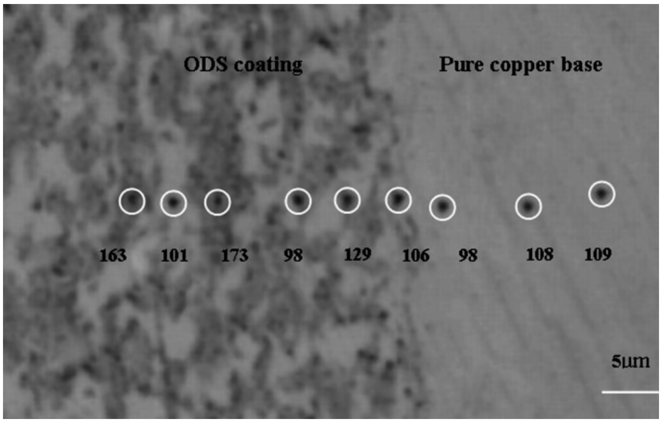

Fig. 8. Variation of micro hardness across the interface.

Regions containing high concentrations of various elements are shown in Fig. 7, obtained using EPMA mapping for cross-section of the interface zone, facilitated to obtain elemental maps for Al and O. The results indicate a fairly uniform distribution of O and Al particles along the coating layer. The regions marked (O), (Al) indicate high concentrations of O and Al; these are consistent with the OM and SEM investigation results which show that dark areas have relatively high Al_2O_3 content.

Fig. 8 shows the hardness value of the copper substrate and the ADS coating layer in the range of 98–109 Hv and 98–173 Hv, respectively. The ADS coating hardness values are much higher than that of the copper substrate because the introduction of Al_2O_3-reinforcing particles to the Cu soft matrix results in an increase in hardness of the coating layer. Improvements in mechanical properties of the composite are due to effective Al_2O_3 particle-dislocation interactions in the copper matrix and also to confining of copper grain boundaries by Al_2O_3 particles. It may be noted that the hardness values presented are uneven in the ADS coating layer. Dark areas with a high Al_2O_3 content showed a high hardness, while bright areas showed a similar hardness with the copper base. It is noteworthy to mention that the uneven hardness values also prove that the high hardness value is due to the action of the Al_2O_3 reinforcing particles, and that pure copper particles maintained their mechanical properties during sintering and underwater shock wave compaction.

Fig. 9 presents the morphology of the specimen fracture. Fig. 9(a) is the fracture surface of the copper substrate, quasi-

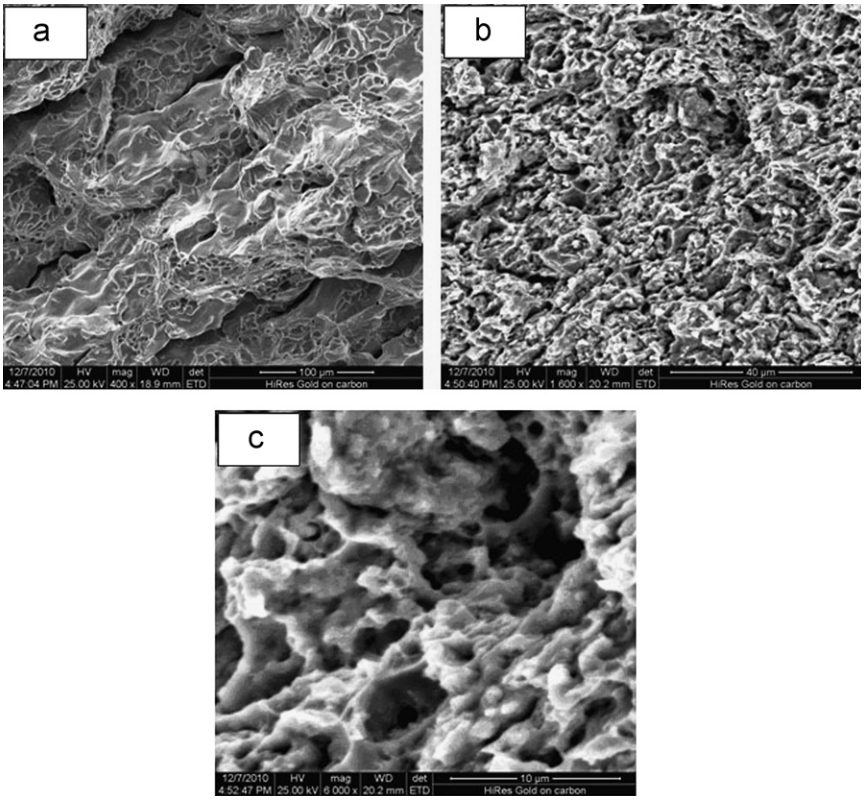

Fig. 9. (a) SEM image of copper base fractography; (b) SEM image of ADS coating fractography; (c) Enlarge SEM image of ADS coating fractography.

cleavage modes, in which shallow dimple fractures can be observed and the quasi-cleavage fracture appearance is predominant. Fig. 9(b), at lower magnification, shows many shallow dimples and cavities on the fracture. The fracture mechanism for ADS coating layer still follows the model of micropore nucleation, growth and accumulation—that is, mainly due to the large differences in properties between alumina particles and copper matrix, cracks will first form on the matrix-particle interface, then will grow and coalesce into voids, and finally, the voids will coalesce into rows and complete fracture will occur [11]. Despite the presence of marked intergranular fracture characteristics and obvious dimples connected like a net as apparent at high magnification in Fig. 9(c), the fine and homogeneous microstructures offer the promise of good toughness, along with high strength.

The sintering and underwater explosive compaction technique thus may be judged as attractive for the fabrication of ADS coatings on copper substrate because of its simplicity, low cost, and controllable coating thickness.

6. Conclusions

ADS coating on copper substrate was produced by ball-milled Cu and powders, pre-compressed, with the coating-substrate cosintered and compacted by underwater explosive. The pre-sintered coating can be green-machined into a desirable shape and dimension. Underwater shock wave dynamic consolidation results in an ultra-rapid consolidation of the sintering powders into bulk materials in a very short duration, and this inhibits recrystallization and grain growth.

1) Microstructure investigation showed that the ADS coating developed after shock compaction had a uniform and fine-grained composite structure with nano-size crystalline. Also, SEM images and element mapping at the interface zone indicated a strong surface bonding between the ADS coating and copper base without separation or cracks.
2) The results indicate that the ADS coating has an obvious higher hardness comparing with the pure copper base, which contributed to the existence of the nano-crystallines. The fracture surface of the ADS coating shows intergranular fracture.

The convenience and low cost of this processing method makes it useful for future studies on the possibility of fabricating thicker and stronger coating on complex substrate surfaces.

Acknowledgments

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