Research Article

Dynamic Deposition of Nanocopper Film on the β -SiC_p Surface by Magnetron Sputtering

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The uniform nanocopper film was deposited on the surface of micron β -SiC particle by magnetron sputtering technology successfully. The surface morphology and phase constitution of the β -SiC particle with nanocopper film were analyzed and dynamic deposition behavior was investigated in detail. The concept of dynamic deposition was put forward to interpret formation mechanism of copper nanofilm on the surface of β -SiC particles.

1. Introduction

In recent, SiC was a key candidate for high temperature applications due to more superior performance for better mechanical and physical characteristics, high specific strength, modulus, and so forth. So it became an attractive choice for reinforcing copper matrix composites [1, 2]. Adding ceramics particles into copper matrix cannot only enhance the mechanical performance but also keep its desirable electrical and thermal conductivity. However, it was difficult to resolve the poor wettability between SiC particle and copper, which limited the wider application scope of copper composites. The surface modification technology was developed in order to improve the interface bonding ability [3], for example, electroless plating, sol-gel and plasma modification, and so on [4–9]. At present, the electroless plating method was researched as the main surface modification route. But the expensive activator cost and complex reaction procedure impeded the industrial application in the great degree. Magnetron sputtering technology was investigated to form thin coating and/or film on the different substrate material [10–12]. The reports about magnetron sputtering film on the surface of ceramics particles were scarce. In present work, β -SiC particles were modified with copper nanofilm. The main purpose of this research was to confirm the validity of magnetron sputtering technology. Other purposes were aimed to survey the impact of the magnetron sputtering process parameter on the growth

and formation of copper film. The third purpose was to investigate dynamic deposition behavior of copper nanofilm.

2. Materials Fabrication and Characterization

The β -SiC particles with average diameter $65\ \mu\text{m}$ were chosen as experiment material. The self-made microparticles magnetron sputtering coating equipment was executed to fabricate the copper film. The circular pure was chosen as sputtering target material and was put on the holder with cooling circulated water device. The β -SiC powder was set into the sample container and the target distance was 170 mm. The vacuum pressure was about 1.2×10^{-3} Pa. The argon gas was introduced into the reaction equipment with flow 20 sccm and sputtering pressure was about 1.0 Pa. Sputtering power was set as 270 W, 370 W, and 420 W and sputtering time was 30 min, 60 min, and 90 min, respectively. The experimental temperature was controlled in $100\sim 200^\circ\text{C}$. The samples holder with low frequency swing and ultrasonic wave with oscillation high frequency was introduced to make the β -SiC particles swirl in order to ensure copper film on the surface of all particles uniform. All the parameters of β -SiC particles and experimental parameter were defined in Table 1.

The phase composition of copper film was identified by X-ray diffraction (D8 Advance), the acceleration voltage was 40 kV, and scan velocity current was 40 mA. The scanning

FIGURE 1: The morphology of SiC particles before and after sputtering: (a) received SiC, (b) S3, and (c) local amplified photo of S3.

TABLE 1: The parameters of β -SiC particles and experimental parameter were listed.

Specimen	Sputtering time	Substrate temperature	Sputtering power
S1	30 min	25°C	370 W
S2	60 min	25°C	370 W
S3	90 min	25°C	370 W
S4	60 min	150°C	370 W
S5	60 min	250°C	370 W
S6	60 min	25°C	270 W
S7	60 min	25°C	440 W

speed was 10°/min and step length was 0.02°. The grain size of copper film was calculated according to Scherrer formula. The morphology of SiC particles with copper film was observed by SEM (FEI-200) and the acceleration voltage was set as 20 kV. The atomic force microscopy (Germany, Dimension Icon) was carried on to analyze the three-dimensional structure. The parameter was as follows, work mode was tapping mode, the scanning scope was about $2\ \mu\text{m} \times 2\ \mu\text{m}$ and sweep frequency was kept in 1 Hz. Three-dimensional topography of the copper film on the SiC particles was analyzed by NanoScope Analysis software. At least 9 lines at different positions in the same area were measured and calculated to research into variation tendency. The geometric model of thin film growth on the surface of SiC particles was put forward according to SEM and AFM results.

3. Result and Discussion

Figure 1 revealed the surface morphology of SiC particles before and after sputtering copper films. The original β -SiC powders had the irregular shape and smooth surface; (see Figure 1(a)). The uniform continuous and compact copper film on the surface of β -SiC powders was detected after dealing with the magnetron sputtering treatment (as seen in Figure 1(b)). From Figure 1(c), the copper film was covered on the surface of SiC particles. The above results proved that magnetron sputtering was effective for depositing the copper film on the β -SiC particles.

TABLE 2: The copper size and proportion of copper on the SiC_p surface under different sputtering conditions.

Specimen	Mass fraction of Cu, %	Grain size (nm)
S1	0.32%	29.86
S2	1.16%	31.08
S3	2.20%	34.37
S4	0.79%	33.42
S5	2.05%	43.80
S6	0.60%	28.37
S7	1.61%	38.08

Figure 2 gave XRD diffraction spectrum of β -SiC powders film in different sputtering conditions. As seen from original SiC powder, the SiC phase can be detected in Figure 2. After magnetron sputtering deposition, the copper phase can be found. We calculated the ratio of Cu/SiC according to the diffraction peak intensity ratio by X-ray quantitative analysis technology. The results were shown in Table 2.

The diffraction peak intensity of the copper increased as the temperature, sputtering power, and sputtering time increased (see Figures 2(a), 2(b), and 2(c)). The increase of SiC powders temperatures resulted in the bigger critical formed nuclear size, so it was easy to form the massive island organization, as the result that the deposition amount of copper was bigger. At the same time, the sputtering threshold of copper was low, high sputtering yield of the copper can be obtained, and high deposition rate can be gained. It was obvious that thicker copper film was easy to obtain as sputtering power and time increased. The diffraction peak of copper film (111) on the β -SiC particles was shown in Figure 2(d). So obvious broad trend of diffraction peak of copper had occurred. This diffraction peak broadened phenomenon can be observed for all sputtered samples. The grain size of sputtering copper was calculated by the Scherrer formula under different sputtering conditions. The grain size in copper film increased with prolonged sputtering time, enhanced sputtering power, and elevated temperature. The copper film was made up of grains size with 20~50 nm.

The morphology of copper film on the surface of β -SiC particles was enumerated in Figure 3. The copper film was composed of bigger grains and vast smaller grains, while

FIGURE 2: XRD diffraction spectrum of β -SiC particles with copper film under different experimental conditions. (a) Substrate temperature (S2, S4, and S5), (b) sputtering power (S6, S2, and S7), (c) sputtering time (S1, S2, and S3), and (d) the diffraction peak spectrum of copper (111) diffraction peak spectrum in S5 specimen.

the bigger grains were composed of dozens of smaller grains with tens of nanometers. The bigger grains were considered as isolated island. As the sputtering time extended, the deposit amount of copper atoms on the surface of β -SiC particles as well as first sedimentary copper film increased. Meanwhile copper formation nucleation rate, growth rate of new nuclear, growth rate of nuclear island, and formation rate of island enhanced as sputtering time increased. As a result, the abundant nanometer grains and island formed at the different rates (Figure 3(b)). The temperature of β -SiC particles was affected by two main factors during sputtering process. One factor was substrate temperature, and the other factor was temperature increment which resulted from impact and collision between β -SiC particles and copper grains. The higher

substrate temperature would improve diffusion capacity of copper atoms and it was a benefit for the formation of thick organization film. Meanwhile, copper atoms with nanometer lever made melting point of copper lower, so the partial meltdown of copper film can occur. The difference of coefficient of thermal expansion between copper and β -SiC particle resulted in higher thermal mismatch stress. So local detachment phenomenon of copper film can be detected (Figure 3(c)). When sputtering yield of copper film increased, sputtering power enhanced. It would accelerate deposition rate of copper film on the β -SiC_p surface, and then island-like agglomeration can be formed quickly (Figure 3(d)).

The three-dimensional size of the island-like big grains was about 200~500 nm. The small grains were about tens

FIGURE 3: The morphology of copper film on the surface of β -SiC particles: (a) S2, (b) S3, (c) S5, and (d) S7.

FIGURE 4: Atomic force scan image of sputtering copper film on the surface of β -SiC particle in S2 sample.

of nanometers. The size of smaller grains was in accordance with computational results according to Scherrer formula. In S2 specimen, surface roughness of copper film on the β -SiC grain was measured. So the root mean square roughness was 33.8 nm and maximum roughness was about 219 nm. Then the average size on the island of 100 nm~400 nm and vertical altitude was 10 nm~80 nm (as Figure 4).

The dynamic deposit process of copper film on the β -SiC particles can be described as follows. It concluded

condensation, nuclei formation, growth of nuclei, formation of island, and connection film from the extension of island. The sputtered copper atoms reached on the surface of β -SiC particle and some copper atoms can be adsorbed onto SiC particle. The partial copper atoms were rebounded by the β -SiC particle (Figure 5(a)). β -SiC particles were kept in motion state and surface morphology became uneven, so it became difficult for adsorption of copper atoms on β -SiC particles. So adsorption rate of copper atoms reduced (Figure 5(b)).

FIGURE 5: The diagram of dynamic deposition process of the nanocopper film on the surface of SiC particle.

As sputtering process continued, the copper atoms could integrate with copper atom on the surface of β -SiC particle to form atomic cluster. The stable critical nucleus began to form as atomic cluster grew up to a certain size (Figures 5(c) and 5(d)). The movement of β -SiC particles shortened migration distance of copper atomic and promoted adsorption and polymerization of sputtering atom on the surface copper atoms of β -SiC particles, and then it improved the speed of critical crystal nucleus to grow up, as shown in Figure 5(e). The smaller island-like structure of the copper atoms can be formed on the surface. As the sputter time was prolonged, critical nucleus of the copper atoms became bigger. The more copper atoms aggregated to form the bigger island-like structure (Figure 5(f)). As sedimentation process continued, network structure film began to form by the mutual contraction of the island bottom. The subsequent copper atoms continued to deposit inside the hole of network structure film. More perpetual cyclic process of the island growth and film formation continued. At last, the continuous film with ten of nanometers gradually formed (Figure 5(g)). The influence factors of the copper films were decided by diffusivity capacity of atomic adsorption and shadow effect of island structure. The above influence factors were obvious during the sputtering process on substrate plate. In present research, β -SiC particles were kept in the motion condition by adjustment of vibration frequency of ultrasonic and oscillation frequency of rack. So the shadow effect of island structure was reduced

into lower level. This effect was obvious during dynamic deposit process for copper film. Dynamic deposition process facilitated the uniform growth of copper film and enhanced compactness of copper film, so it improved copper film quality. Based on above analysis, we can come to a conclusion that dynamic formation mechanism of copper film was a mixture of main island structure growth and secondary layered structure growth as the β -SiC particles moved during the process of sputtering.

4. Conclusion

In this paper, the dense and continuous copper film with nanometer level had been obtained on the surface of β -SiC grains by magnetron sputtering successfully. The dynamic deposit process of copper film on the β -SiC particle concluded condensation, nuclei formation, growth of the nuclei, formation of island, and connection film from the extension of the island. Dynamic deposition process facilitated the uniform growth of copper film. Dynamic formation mechanism of copper film was a mixture model of main island structure growth and secondary layered structure growth as the β -SiC particles moved during the sputtering process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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