Paper

Thermal and Mechanical Properties of Harmonic-Structured Composite with Copper and Molybdenum

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ABSTRACT

Cu–Mo harmonic-structured composite was produced via mechanical milling (MM) followed by spark plasma sintering (SPS), and its thermal and mechanical properties were investigated in detail. Microstructural observation of the MM powders and SPS compacts was achieved using scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS). The mechanical properties of the SPS compacts were evaluated using results of the Vickers hardness test. The thermal properties of them were evaluated using results of thermo-mechanical analysis and laser flash method. SEM/EDS micrographs profile indicated that the Cu–Mo harmonic-structured composite has the network region composed of molybdenum and the dispersed region of copper. The Cu–Mo harmonic-structured composites demonstrate low coefficient of linear expansion and enough thermal conductivity compared to the conventional Cu–Mo particle dispersed composite. The hardness of Cu–Mo harmonic-structured composite corresponds to the Voigt model of the rule of mixture of Cu and Mo. The harmonic structure control is effective for an improvement of the thermal and mechanical properties.

KEY WORDS

harmonic structure, coefficient of linear expansion, thermal conductivity, mechanical milling, spark plasma sintering

1 Introduction

In recent years, integrated circuits (IC) have been miniaturized with the miniaturization of electronic devices. The amount of heat generated by the high-density and high-power output has increased than ever before. Therefore, a heat spreader with high thermal conductivity effectively move the heat from a heat source¹⁾. The thermal properties of both low coefficient of thermal expansion (C.T.E.) and high thermal conductivity are favored as the heat spreader materials, because the IC mainly consists of a silicon with low C.T.E. A copper is suitable for heat spreader materials for the high thermal conductivity in metals, but the C.T.E. is larger than that of the semiconductors. The large difference of C.T.E. causes a separation between semiconductor and heat spreader for a cyclic thermal stress. On the other hand, the C.T.E. of molybdenum is close to that of the silicon and the molybdenum has higher thermal conductivity than the silicon. A Cu–Mo composite with the low C.T.E. and high thermal conductivity comparatively is suitable as the heat spreader materials. However, in Cu–Mo composite, increase of the Cu rate induces high C.T.E. and high thermal

conductivity. On the contrary, increase of the Mo rate induces low C.T.E. and low thermal conductivity. Therefore, it is difficult to introduce the thermal properties of the low C.T.E and high thermal conductivity simultaneously in the Cu–Mo composite materials. The low C.T.E and high thermal conductivity is trade-off relationship in Cu–Mo composite. Whereas, the harmonic-structured materials simultaneously demonstrate two mechanical properties in the trade-off relationship, for example of the high strength and high ductility²⁾. The harmonic structure has a possibility that suppressing the trade-off relationship can be introduced to the Cu–Mo composite. However, the research on the thermal properties of harmonic-structured materials have not yet. In this paper, the Cu–Mo harmonic-structured composite is produced via the mechanical milling (MM) followed by the spark plasma sintering (SPS), and its thermal and mechanical properties are investigated in detail.

2 Experimental

Pure copper powder (99.7 mass% purity; Nippon Atomized Metal Powders Corporation) and pure molybdenum powder (99.9 mass% purity; Kojundo Chemical Laboratory Co., Ltd.) were used in this study. The initial particle sizes of the pure Cu and the pure Mo

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powders were approximately 80 and 3.0 μm , respectively. These powders were mechanically milled using a planetary ball mill (P-6; Fritch Co., Ltd.) with an SKD11 vessel and SUJ2 steel balls in Ar atmosphere at room temperature. Mixed powder consisting of pure Mo and pure Cu (50.0 to 80.0 mass%) was mechanically milled at a ball-to-powder weight ratio of 1:2, an MM time of 86.4 to 172.8 ks and a rotation speed of 200 and 250 rpm. The mechanically milled powder containing pure Cu and Mo was sintered using an SPS apparatus (SPS-510L; Sumitomo Coal Mining Co., Ltd.) at 1173 K and 100 MPa for 1.8 ks. Scanning electron microscopy (SEM) / energy dispersive X-ray spectroscopy (EDS) were employed to observe the microstructure of the SPS compact. The mechanical properties of the SPS compacts were evaluated by the Vickers hardness test (VMT-7; Matsuzawa Co., Ltd.) using an indenter with the load of 196.1 N. The thermal properties of them were evaluated by the thermo-mechanical analysis (TMA: SS6100, NIS nano technology Co., Ltd.) at temperature elevation rate of 0.17 K/s under Ar atmosphere and laser flash method (LDA447 Nanoflash, Netzsch Co., Ltd.).

3 Results and discussion

The MM powder in which pure Cu and pure Mo powders were combined by MM for 172.8 ks is shown in Fig. 1. Figs. 1 (a) and (b) show SEM micrographs of the appearance and cross section of the MM powder with Cu (70.0 mass%), respectively. Figs. 1 (c) and (d) indicate EDS results for the Cu and Mo concentrations in the cross section shown in Fig. 1 (b), respectively. The MM powder shown in Fig. 1 (b) exhibits a different contrast in the surface and inner regions, and Figs. 1 (c) and (d) demonstrate that the surface region has high Mo concentration. The shell/core powder as shown in Fig. 1 was sintered using an SPS apparatus, and an interesting microstructure was obtained. Figs. 2 (a), (b), (c) and (d) show this microstructure in SEM micrographs of the SPS compacts of the shell/core powders with the Cu in the mass fraction of 80, 70, 60 and 50%, respectively. Relative densities for each SPS compact are also shown in Fig. 2. Each SPS compact has an enough sintered density for the relative density of approximately 99%. These micrographs have a network structure with Mo material shown by a bright contrast, and its network region corresponds to the surface region of the MM powder shown in Fig. 1. The network width increases with decreasing the mass fraction of Cu. The dispersed region surrounding the network corresponds to Cu material. A microstructure having network and dispersed regions is referred to as a “harmonic structure.”

Fig. 3 demonstrates coefficient of linear expansion at 373 K to 1073 K of the harmonic-structured composites with 50.0 to 80.0 mass% Cu and only Cu and Mo SPS compact. The changes in the coefficient of linear expansion from 323 K to 1073 K of the harmonic-structured composites with less than 70.0 mass% Cu are very small compared to that with 80.0 mass% Cu. Fig. 4 shows

Fig. 1 SEM micrographs of the appearance (a) and the cross section (b) and the EDS elemental mapping results for Cu (c) and Mo (d) of the MM powder with Cu mass fraction of 70.0%.

coefficient of linear expansion of the harmonic-structured and particle dispersed composite³⁾ with 70.0 mass% Cu. The particle dispersed composite is conventional Cu–Mo composite consisting of Cu matrix and dispersed Mo particles^{1,4)}. The coefficient of linear expansion of the particle dispersed composite increases with increasing temperature. On the other hand, the coefficient of linear expansion of the harmonic structured composite does not change

Fig. 2 SEM micrographs of the harmonic-structured composites sintered by SPS from the MM powders with the Cu mass fraction of 80.0 (a), 70.0 (b), 60.0 (c) and 50.0% (d).

even if temperature increase. Fig. 5 demonstrates the coefficient of linear expansion of the harmonic-structured and conventional particle dispersed composite⁴⁾ in the change of Cu mass fraction at 423 K, which is a temperature comparable for the literature value. Each Cu–Mo composite decreases with decreasing Cu mass fraction. However, the harmonic-structured composite has the lower coefficient of linear expansion than particle dispersed

Fig. 3 Coefficient of linear expansion of the harmonic-structured composites with the Cu mass fraction of 50.0 to 80.0% at 373 to 1073 K.

Fig. 4 Coefficient of linear expansion of the harmonic-structured and the particle dispersed composites with the Cu mass fraction of 70.0% at 373 to 1073 K.

Fig. 5 Coefficient of linear expansion of the harmonic-structured and the particle dispersed composites with the Cu mass fraction of 50.0 to 80.0% at 423 K.

composite in low Cu mass fraction area. These results reveal that harmonic-structured composite has excellent coefficient of linear expansion compared to conventional particle dispersed composite.

Fig. 6 Thermal conductivity of the harmonic-structured and conventional particle dispersed composites with the Cu mass fraction of 50.0 to 80.0%.

Fig. 7 Relationship between thermal conductivity and coefficient of linear expansion in the harmonic-structured and particle dispersed composites with the Cu mass fraction of 50.0 to 80.0%.

The low coefficient of linear expansion of the harmonic-structured composite is attributed to the restriction for the thermal expansion of Cu by the network structure of Mo.

Fig. 6 shows the thermal conductivity of the harmonic-structured and conventional particle dispersed composite⁴⁾ in the change of Cu mass fraction. The thermal conductivity of the harmonic-structured composite is slightly lower than the particle dispersed composite. However the difference in the thermal conductivity between the harmonic-structured and particle dispersed composite is quite small. It is less than 7%. Decrease of thermal conductivity of the harmonic-structured composite is attributed that the Cu area with high thermal conductivity is not continuously connected in the harmonic structure. Fig. 7 demonstrates the relationship between thermal conductivity and coefficient of linear expansion in the harmonic-structured and particle dispersed composite⁴⁾. Even though the harmonic-structured composite with 60.0 mass% Cu and the particle dispersed composite with 50.0 mass% Cu have almost the same coefficient of linear expansion, the thermal conductivity of the harmonic-structured composite is higher than that of the

Fig. 8 Vickers hardness of the harmonic-structured composites with the Cu mass fraction of 50.0 to 80.0%.

particle dispersed composite. Therefore, in the case of Cu–Mo composite, harmonic structure can improve the thermal properties with the trade-off relationship between thermal conductivity and coefficient of linear expansion.

Fig. 8 shows the relationship between the Vickers hardness and Cu mass fraction. The Vickers hardness of the harmonic-structured composites with 50.0 to 80.0 mass% Cu corresponds to the value of Voigt model of the rule of mixture. In general, the hardness of the particle dispersed composites is lower than the Voigt model and higher than Reuss model of the rule of mixture⁵⁾. High hardness of the harmonic-structured composites is attributed to the restriction by the network structure of Mo with high rigidity.

4 Conclusion

A harmonic-structured Cu–Mo composite with a network region of pure Mo and a dispersed region of pure Cu was fabricated by a mechanical milling and spark plasma sintering process. Thermal and mechanical properties of the harmonic-structured Cu–Mo composite were subsequently evaluated. The combined powder with a surface of pure Mo and an inner region of pure Cu was produced by the mechanical milling process. As this combined powder underwent spark plasma sintering, the harmonic-structured Cu–Mo composite with a network region of pure Mo and a dispersed region of pure Cu was fabricated. The harmonic-structured Cu–Mo composite demonstrates high thermal conductivity in spite of almost the same coefficient of linear expansion compared to the conventional particle dispersed Cu–Mo composite. The hardness of the harmonic-structured Cu–Mo composite corresponds to the Voigt model of the rule of mixture of Cu and Mo.

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