Development of Cr-Cu Heat-Sink Composite Materials for Semiconductor Devices

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Chromium-copper composite materials have been developed for heat-sink applications of high power devices. Tungsten-copper and molybdenum-copper composites, with low thermal expansion coefficient and high thermal conductivity, have been used for the applications. These materials have poor formability and poor machinability, which raise processing costs. Tungsten and molybdenum powder are both rare metals, very expensive, and have unstable supply. Chromium is the same 6A group element as W and Mo, and the cost of its powder is lower and its supply is more stable, but its thermal properties are inferior to those of W and Mo. Three original processes have been developed to realize thermal properties of Cr-Cu close to those of Mo-Cu and W-Cu: 1) secondary precipitation heat treatment, 2) rolling and 3) cladding with Cu and rolling. The developed composites could have high cost effectiveness for processing the heat-sink parts owing to the excellent properties for rolling ability, pressing formability and machinability.

Keywords: Heat-sink composite material, Thermal conducting materials, Powder metallurgical processing, Chromium-copper (Cr-Cu), Cr-Cu/Cu clad and rolled, Elongated and flattened Cr structure, Pressing, Thermal expansion coefficient, Improvement of thermal properties.

1. Introduction

There are some types of heat-sinks or heat-spreaders such as a well-known fin shape made of Aluminium. The heat-sink referred in this paper is used for high power semiconductor chip made of such as Silicon, SiC and GaAs or module in the device for optical fiber communication, wire-less communication, an inverter controller and so on. In order to dissipate heat from a semiconductor chip to outside smoothly, a heat-sink is soldered or brazed with both a semiconductor chip and AlN substrate, Al₂O₃ substrate or a case made of Kovar(Fe-Ni-Co alloy) directly. For a heat-sink, low thermal expansion coefficient is required to close to that of the jointed material, in addition to high thermal conductivity. Molybdenum-copper (Mo-Cu) ¹ ² and tungsten-copper (W-Cu) ³ ⁴ have been used for these applications. These are produced by P/M processes. Tungsten (W) or molybdenum (Mo) powder is compacted and sintered, and then infiltrated with copper (Cu). W and Mo are not dissolved in Cu. Therefore, W-Cu and Mo-Cu could be said composite materials. These materials have a low thermal expansion coefficient in the range of 6.5 to 9 × 10⁻⁶/K and 7 to 14 × 10⁻⁶/K respectively. However W and Mo powder are both rare metals, very expensive and unstable to be supplied because the ores are mined small in quantity from a limited area. Furthermore, the poor deformability and poor machinability of these materials become high processing costs for making heat-sink parts.

Chromium (Cr) is also a strong candidate for the heat-sink application, because it is the same 6A group element as W and Mo. Its powder price is lower and more stable, because the ore is mined much more in quantity than W and Mo, and Cr is widely used for such as stainless-steel. But thermal properties of Cr are a little inferior to W and Mo as shown in Fig.1. Fig.1 also shows the thermal properties of W-Cu, Mo-Cu and chromium-copper (Cr-Cu) composites calculated by the German’s model ⁵. It is shown that Cr-Cu can not be substituted for W-Cu and Mo-Cu in thermal properties from the simply calculated results. We investigated three approaches: 1) secondary precipitation heat treatment, 2) rolling and 3) cladding with Cu and rolling, to improve enough thermal properties of Cr-Cu to substitute successfully for W-Cu or Mo-Cu used in the heat-sink application.

![Graph: Relationship between thermal conductivity and thermal expansion coefficient](image)

**Fig. 1**: Relationship between thermal conductivity and thermal expansion coefficient at 323 K to 673 K.

2. Discovery of decrease of thermal expansion coefficient by secondary Cr precipitation heat treatment

Chromium is dissolved with Cu slightly, as chromium copper alloy (JIS-Z3234): 0.4-1.2mass%Cr-Cu used for an electrode is well known as a precipitation hardened alloy.

The developed Cr-Cu composites are also produced by P/M process followed by infiltration with Cu. However Cr is dissolved in Cu phase up to approximaty 3mass% during the infiltration with Cu at 1473K. Therefore secondary precipitation treatment is necessary for better thermal conductivity. We found the secondary precipitation heat treatment that not only thermal conductivity but also thermal expansion coefficient could be improved.

Used Cr powder was made by crushing and shifting through a sieve having 150 µm mesh size from high purity Cr by electric furnace refining method. The Cr powder was compacted and sintered at 1773K for 3.6ks in Hydrogen. The sintered Cr porous compact is infiltrated with Cu at 1473K for 1.8ks in Hydrogen and then cooled slowly. And/or the Cr-Cu infiltrated compact is solution treated at from 1173K to 423K followed by cooling slowly. And then it is aged at from 773K to 1023K. Through this procedure, dissolved Cr in Cu phase is secondary precipitated as
nanometer level particles. The secondary precipitated Cr could contribute to make thermal expansion coefficient of Cr-Cu lower without hardening. Fig.2 shows relationship between aging temperature and thermal expansion coefficient on 50mass%Cr-Cu material. The drastic decrease of thermal expansion coefficient was discovered in the bottom at 823K. The phenomenon was estimated to relate to larger warp contrast by coherent Cr precipitate at 823K. Thermal properties of the developed Cr-Cu materials by the precipitation treatment could be close to those of W-Cu or Mo-Cu. Furthermore, in order to substitute Cr-Cu for W-Cu or Mo-Cu, we tried two other approaches to improve much more in thermal properties. One approach is to control Cr-Cu structure using cold rolling, and another is cladding Cr-Cu with Cu and subsequent rolling.

3. Effect of cold rolling of Cr-Cu on thermal properties

To obtain the sufficient rolling deformability, pore free and inclusion free structure of Cr-Cu infiltrated compact is identified to be essential. Carbon and oxygen contents of sintered Cr have an effect on the infiltration ability. For the pore free and inclusion free structure, carbon content and oxygen content of sintered Cr should be lower than 0.01 mass% respectively. In the rolling test of 50mass%Cr-Cu material, the pore free and inclusion free material showed good cold rolling formability. However some micro cracks were observed on the surface of the rolled sheet, and these cracks were detrimental to Ni plating. These micro cracks appeared mainly at the boundaries between Cr phase and the Cu matrix. A single-phase Cr shows generally brittle fracture at the temperature lower than around 350K. Warm rolling at over 335K with appropriate rolling conditions was effective for reducing the cracks and confirmed to be used for the applications. 50mass%Cr-Cu material could be rolled up to the reduction rate over 95% without intermediate annealing. Fig. 3 shows the cross-sectional structure. In the rolled Cr-Cu material, Cr phases are significantly elongated and flattened, resembling a fibrous structure. Fig.4 shows the effect of reduction rate of rolling on thermal expansion coefficient of 50mass%Cr-Cu. Such a fibrous structure of Cr phases makes the thermal expansion coefficient much lower than 13.0 × 10⁻⁶/K predicted from the rule of mixture. While the flattened Cr structure promotes thermal conductivity in the in-plane direction, both rolling direction and transverse direction. It deteriorates it in the thickness direction as shown in Fig.5.
4. Effect of Cr-Cu clad with Cu on thermal properties

For some of heat-sink applications, thermal flow along the thickness direction is mainly required. In order to improve the thermal conductivity in the thickness direction without raising the thermal expansion, we investigated Cr-Cu infiltrated compacts or rolled sheets were bonded with Cu sheets and rolled. Hereafter this clad material is named Cr-Cu/Cu clad & rolled. Fig.6 shows cross-sectional structure of Cr-Cu/Cu clad & rolled.

50mass%Cr-Cu infiltrated compacts or rolled sheets and pure Cu (C1020P) sheets were stacked alternately and diffusion bonded at 1173K under the pressure of 20MPa for 2.4ks by Spark Plasma Sintering (SPS). Then the clad material was cross-rolled at 373K up to 97% of reduction rate.

Fig.6 Cross-sectional structure of Cr-Cu/Cu clad & rolled.

Fig.7 shows relationship between thermal conductivity and thermal expansion coefficient on Cr-Cu/Cu clad & rolled materials compared with Cr-Cu rolled materials. The Cr-Cu/Cu clad & rolled materials were made by changing the thickness ratio of 50mass% Cu-Cu and Cu, and the Cr-Cu rolled materials were made by changing the content ratio of Cr and Cu. The density of these materials varied from 8.35g/cm³ to 8.52g/cm³ and from 7.95g/cm³ to 8.21g/cm³ respectively. From this figure, it can be seen the thermal conductivity of Cr-Cu/Cu clad & rolled materials are improved approximately 70Wm⁻¹K⁻¹ in the both directions higher than Cr-Cu rolled materials.

Fig.8 shows relationship between thermal conductivity and density, and Fig.9 shows relationship between thermal expansion coefficient and density on Cr-Cu/Cu clad & rolled and Cr-Cu rolled materials. Thermal conductivity of both Cr-Cu clad & rolled and Cr-Cu rolled have identical liner relation to density; Cu content ratio in rolling direction and thickness direction respectively. However thermal expansion coefficient of Cr-Cu clad & rolled and Cr-Cu rolled have individual liner relation to density. So these figures show the Cr-Cu/Cu clad & rolled could improve thermal conductivity in the thickness direction without degrading the thermal expansion coefficient in the rolling direction. The suppression of the thermal expansion coefficient of Cr-Cu/Cu clad & rolled is thought to be owed to the restraint of Cr-Cu rolled layers on Cu plates of the clad, as Cu phase is restrained by the fibrous structure of Cr phase in Cr-Cu rolled layers⁹.

Fig.8 Relationship between thermal conductivity and density on Cr-Cu/Cu clad and rolled, and Cr-Cu rolled materials.

Fig.9 Relationship between thermal expansion coefficient and density on Cr-Cu/Cu clad and rolled, and Cr-Cu rolled materials.

5. Conclusion

Fig.10 shows relationship between thermal expansion coefficient and temperature from 323K to 1173K on Cr-Cu/Cu clad & rolled materials, 50mass%Cr-Cu infiltration compact and the Cr-Cu rolled material. And thermal expansion coefficient of Cr, Cu and these materials calculated by the rule of mixture are also plotted on
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thermal properties of Cr-Cu/Cu clad & rolled materials plotted on the Fig.1. The three approaches that we investigated and invented have made thermal properties of Cr-Cu composite materials close to those of W-Cu and Mo-Cu enough to be applied for the heat-sink.

These developed Cr-Cu composite materials show high rolling ability, cold press formability, machinability and Ni plating ability. By not only using low-cost raw material but also making process cost lower, the composite materials have high cost competitiveness for the heat-sink applications.

The composite materials have been successfully applied for the heat-sink parts for optical fiber communication and for high frequency communication instead of W-Cu and Mo-Cu. Fig. 12 shows the example of the Cr-Cu heat-sink part. We are developing other applications of heat-sink for such as inverter controllers.

**REFERENCES**


**Fig. 10** Relationship between thermal expansion coefficient and temperature on Cr-Cu/Cu clad and rolled materials, as infiltrated Cr-Cu and rolled Cr-Cu compared with related data of rule of mixture.

**Fig. 11** Relation between thermal expansion coefficient and a thermal conductivity on developed Cr-Cu materials for heat-sink application compared with W-Cu and Mo-Cu.

**Fig. 12** An example of Cr-Cu heat-sink part used for optical fiber communication.