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Effect of Copper Family Elements on Phase Transformation of Iron Silicides

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It is known that Cu addition promotes the phase transformation from the metallic to the semiconductor phase of iron disilicide, viz., β-$FeSi_2$. It has, however, not been known of (1) detailed mechanisms of this effect, and (2) the effects of other Cu family elements. In this work, investigations are made on the effects of Au and Ag, as well as Cu, to the metal-to-semiconductor transformation. The fine ceramics technology is utilized to produce some types of Mn-doped iron disilicide added with various amounts of Au, Ag, and Cu. The specimens were heat-treated at 800℃ for various duration of 1 to 36 hrs, or at temperatures from 790 to 950℃ for two hours. The amounts of β-$FeSi_2$ yielded by this heat-treatment were estimated from the results of the measurements of the resistivities and the thermoelectric powers, and the XRD observation.

Key words: iron disilicide, ceramic technology, copper doping, thermoelectric properties

1. INTRODUCTION

β iron disilicide ($FeSi_2$) is a semiconductor, whose conduction type can readily be changed into p-type by doping with Mn or Al, while into n-type by doping with Co. These doped β-phase materials possess a high thermoelectric power and they are superior in the heat- and oxidation-resistances, so that they applicable in a usual atmosphere uses at high temperatures. They also possess a number of practical advantages; i.e., sufficient performances can be achieved by using low purity raw materials because of less structure-sensitivity, and a high cost-performance can be realized by utilizing the conventional ceramics technology.

At 986°C $FeSi_2$ shows a phase transition: the low temperature β-phase (semiconductor) changes into the high temperature α-phase (Fe_2Si_5) plus ε-phase (FeSi) [1]. Iron disilicides prepared simply by melting or sintering include a rather amount of metallic phases. Heat treatment is necessary to obtain a sufficient amount of β-phase. It is known that the heat treatment for 100 hours at 800°C should be carried out to achieve the perfect β-phase transition. It is, however, reported recently that Cu addition can drastically shorten the heat treatment duration required [2,3].

In our laboratory, U-shaped p-n junction devices have produced from $FeSi_2$, with addition of Cu, by using cold pressing and pressure-less sintering, and they are investigated on the effect of Cu addition to the heat treatment duration. The as-sintered $FeSi_2$ samples without Cu were still in the metallic phase, while the thermoelectric power of the Cu-added sample increased with increasing amount of Cu. The output voltage of the as-sintered Cu-doped sample showed a high output of 240~280 mV at a temperature difference of 800 degrees, which suggested that a sufficient amount of semiconductor phase was carried out. The sample added with 1wt% Cu was successfully transformed into the semiconductor phase after the heat treatment of 8 hours at 800°C. It showed the output voltage of 394 mV and the maximum power of 220 Wm/m^2 [4]. These facts suggest a great deal of cost reduction.

In this work, the Cu-addition effect to the β-phase production process required for thermoelectric application are examined by measurements of the resistivities and the thermoelectric powers, and the XRD experiments. The effects are also examined for the other copper family elements, viz., Au and Ag.

2. EXPERIMENTAL

2.1 Production of sintered iron disilicide materials

Figure 1 shows the production process of the sintered iron disilicide materials.

The raw materials were 3N electrolytic Fe, 6N single crystal Si, 3N electrolytic Mn, and 4N oxygen-free Cu. A certain amount of Mn was cleaned with ethanol containing 5% HCl. The specimens were prepared in the constitution of $Fe_{0.92}Mn_{0.08}Si_{2.1}$ and added with 0, 0.1, 0.5, or 2wt% Cu. The Mn content was adjusted at x=0.08, considering the power factor and the

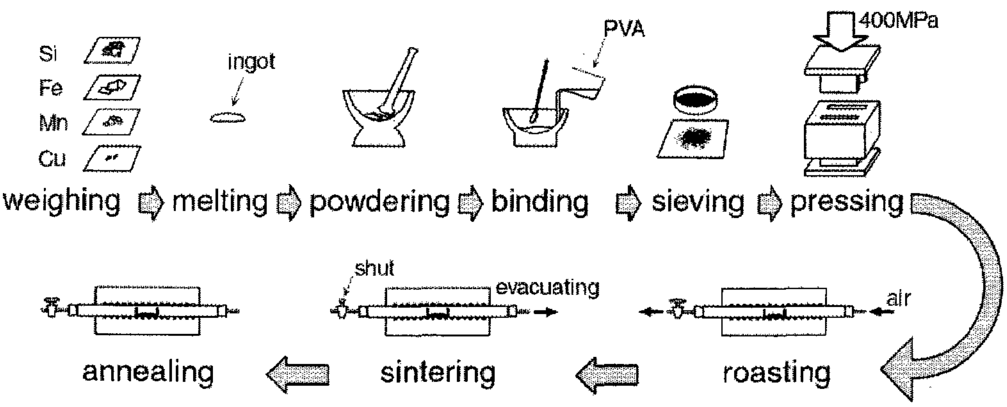

Fig.1 Process of $FeSi_2$ sintered material.

solidification limit of Mn in the sintered $Fe_{1-x}Mn_xSi_2$ [5]. The Si content was adjusted at a slightly larger value than the required amount, considering the reduction in the arc-melting and powdering processes. Arc-melting was performed in an Ar atmosphere to obtain an ingot.

The ingot was grinded into powder with an average diameter of 3 μm. The powder was changed into slurry by adding some poly vinyl alcohol (PVA) solution, and it was dried by stirring and heating. After adjusting the contents of water and PVA at 10wt% or 1wt%, it was temporarily formed into a rod under a pressure of 176 MPa. It was grinded and sieved to obtain particles with a diameter of 180~355 μm.

They were filled into a 30 mm × 4 mm rectangular die and pressed under a pressure of 400 MPa to be formed into a green sample with an apparent density above 60%.

The green sample was put into an aluminous boat, and the boat was placed in an electric furnace. To remove the PVA, the temperature in the furnace was raised up to 400°C with a rising rate of 80°C/h. The inside of the furnace was evacuated by a rotary pump, the temperature was again raised up to 1150°C with a rate of 200°C/h. That temperature had been held for 5 hours, and then the furnace was cooled gradually. Through similar procedures, samples added with Au and Ag were also prepared.

Several specimens in size of 4 mm × 4 mm × 8 mm were cut out of the sintered material obtained. The surfaces of the specimens were polished with SiC polishing paper. The density was measured by the buoyancy method. The density measured was divided by the ideal density of $FeSi_2$ to determine the relative density. Each specimen was annealed isothermally at 800°C for various durations of 1 to 36hrs, and annealed isochronally for two hours at temperatures from 790 to 950°C. Usual powder XRD observation was applied to both the specimens with and without Cu-addition. The observation was performed with Cu-Kα X-rays for the diffraction angle 2θ from 15 to 30 degrees.

2.2 Measurement of resistivity and thermoelectic power

Resistivities were measured at room temperature on the basis of the four-terminal method. The oxides on the surface were removed by polishing, before the terminals were connected. Applying a current of ±50~100mA, the potential difference was measured at the middle of the specimen (4 mm × 4 mm × 8 mm) with a distance between terminals of 3 mm.

Thermoelectric properties were measured at room temperature. One end of the specimen was heated by a small heater to apply a temperature difference ΔT of the order of several K in the longitudinal direction. The values of the thermoelectric power E_0 were measured for a certain temperature differences to obtain the E_0-T curve. The thermoelectric power was determined from the gradient of the curve.

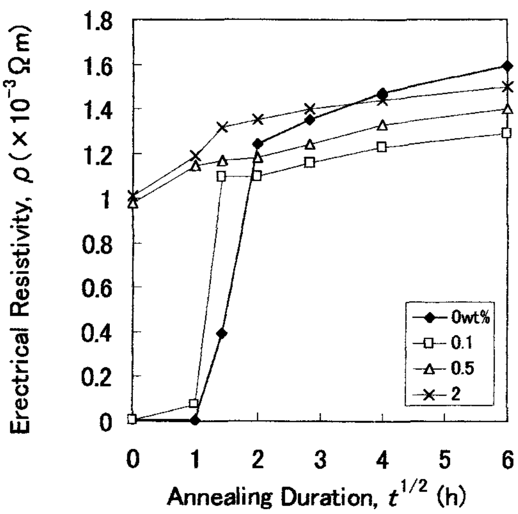

Fig.2 Annealing duration dependences of the resistivities in the sintered eutectic alloys of $Fe_{0.92}Mn_{0.08}Si_2$ added with 0 to 2wt% Cu for the isothermal annealing at 800℃.

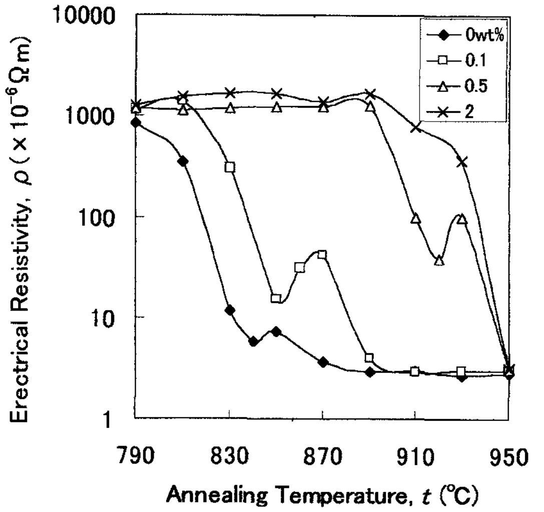

Fig.3 Annealing temperature dependences of the resisitivities in the sintered eutectic alloys of $Fe_{0.92}Mn_{0.08}Si_2$ added with 0 to 2wt% Cu for the isochronal annealing for two hours.

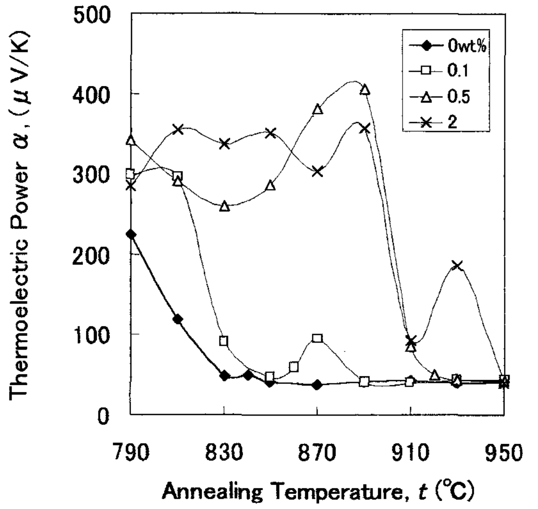

Fig.4 Annealing temperature dependences of the thermoelectric powers in the sintered eutectic alloys of $Fe_{0.92}Mn_{0.08}Si_2$ added with 0 to 2wt% Cu for the isochronal annealing for two hours.

3. RESULTS AND DISCUSSION

3.1 Effects of heat treatment and Cu addition to the resistivity

The amount of the semiconducting β-phase produced can be estimated from the observed resistivities. Figure 2 shows the heat-treatment duration dependences of the resistivities observed after 800°C heat treatment for the specimens added with 0, 0.1, 0.5 and 2 wt% Cu. For the Cu contents equal to and above 0.5wt%, the resistivities of the as-sintered specimens were of the order of 10^{-3} Ωm, while for 0.1wt% and below, they were of the order of 10^{-6} Ωm. This fact suggests that the β-phase is formed by sintering in the specimens containing 0.5wt% or more Cu. The resistivity rapidly increased after the 1-hour heat treatment for the 0% and 0.1% Cu-added specimens, while the slope for the 0.1% case is greater than that for the 0% case, which fact suggests that even a trace of Cu, the transformation to the β-phase are effectively accelerated. Since the increasing rate of the resistivity of the Cu-added specimen after 4h ($t^{1/2}$ = 2) is smaller than that of the specimen without Cu, it is suggested that the resistivity of the Cu-added specimen saturates more rapidly than that of the specimen without Cu. It might be considered that a liquid phase appears due to the lowering of the liquidus temperature by Cu addition to promote the phase transformation. Any explicit evidence has, unfortunately, not been obtained to confirm such a mechanism yet. For samples with Au and Ag, unfortunately, no significant effects were observed from the experiments above.

The relative densities of the specimens were determined, assuming the resistivity differences among the specimens at 36h ($t^{1/2}$ = 6) were caused by the density differences. The results are shown in Table I. The relative densities decreased with increasing amount of Cu addition, which suggests that Cu-addition suppresses the grain growth. The resistivities of the Cu-added specimens increased with the relative densities, which fact suggests the boundary scattering. The resistivity of the specimens without Cu, however, was greater than that of the Cu-added specimens, although the relative density of the specimen without Cu was 96.0%, which is greater than that of the Cu-added specimens. The reason of this fact is now under investigation.

Table I Relative densities of the $Fe_{0.92}Mn_{0.08}Si_2$ added with 0~2wt% Cu.

Amount of Cu (wt%)	Relative density (%)
0	96.0
0.1	93.9
0.5	91.8
2	90.6

Nishida has reported that the temperature dependence of the resistivities in the sintered $FeSi$-Fe_2Si_5 shows a notch at 840~860°C, and that the β-phase is more effectively formed and a lower resistivity is obtained below that temperature [6]. Therefore, the temperature T_c at which the resistivity reaches the maximum in the heat treatment below the notch is the optimum temperature of transformation from the high temperature metallic (ε+α)– to the low temperature semiconducting β-phase.

Figure 3 shows the relation between the heat treatment temperature and the resistivity for the specimens with and without Cu for duration of 2 hours at various temperatures of 790~950°C.

Figure 4 shows the relation between the heat treatment temperature and the thermoelectric power α. For specimens with 0.1wt% or less amount of Cu, peaks existed at 810°C and 870°C, and discontinuities also existed in the temperature-vs.-resistivity curve of the Cu-added samples. T_c increased with the increasing amount of Cu. Similar results were obtained for the thermoelectric power. It is generally known that Cu is useful catalyst acting with d-holes created by the $3d$ to $4s$ transition. It is suggested from the results obtained that Cu acts as catalyst in the decomposition (α→β+Si) process of iron disilicide.

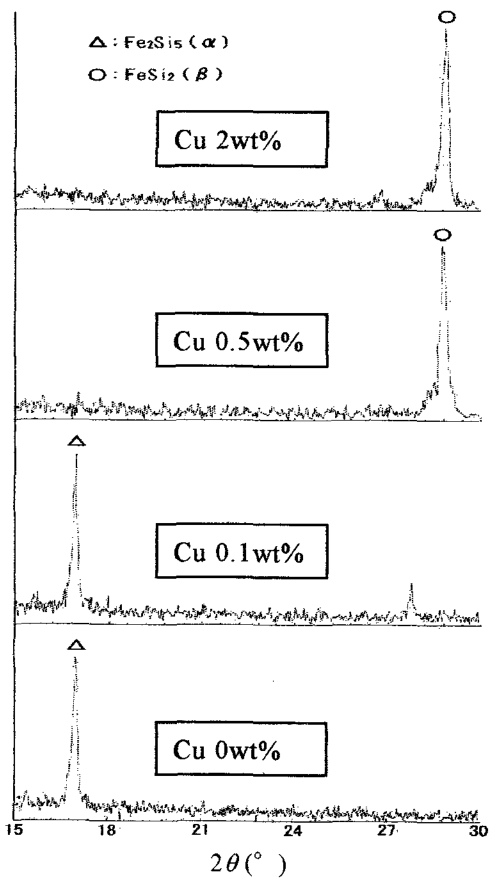

Fig.5 X-ray diffraction profiles of the $Fe_{0.92}Mn_{0.08}Si_2$ sintered materials added with 0 to 2wt% Cu.

3.2 The relation between the resistivity and the phase identified by the X-ray diffraction experiment

Figure 5 shows the X-ray diffraction profiles of the as-sintered specimens, namely the specimens before heat treatment. For the specimens doped with 0 and 0.1wt% Cu, the peak corresponding to the metallic α-phase exists at the diffraction angle of 17 degrees and the resistivity shows a very small value of the order of 10^{-6} Ωm, which is of the order of the resistivity obtained in the case of the specimen without Cu after 36-hour heat treatment at 800°C. It is found from these facts that the semiconductor β-phase can be formed without the heat treatment by adding a trace of Cu.

4. CONCLUSION

It is concluded from the results above as follows:

(1) Cu addition accelerates the decomposition: α→β+Si.
(2) Cu addition is also effective for producing β-phase at higher temperatures than the α-to-β transformation temperature, 860℃.
(3) No significant effects are observed for Au and Ag under the conditions effective for the reaction with Cu.
(4) It is suggested that the reaction with Cu is promoted through the d-holes formed by the electron transition from $3d$ to $4s$ orbital of Cu atoms.

REFERENCES

[1] J.P. Piton, M.F. Fay, *C. R. Acad. Sci.*, **C266**, 514-516 (1968).
[2] H. Ito, H. Nagai, T. Tanaka, S. Katsuyama, K. Majima, Mater. *Trans. JIM*, **41**, 857-864(2000).
[3] Y.K. Hsu, J.J. Wang, C.S. Chang, S.C. Wang, Jpn. *J. Appl. Phys.*, Part 1, **41**, 3854-3859 (2002).
[4] K. Murata, Y. Tsukada, H. Kawarai, A. Matsunawa, M. Kato, I.J. Ohsugi, T. Kojima, I.A. Nishida, in Proceedings of *TEC 2002*, Tokyo, July, 116-117 (2002). (in Japanese).
[5] T. Kojima, M. Sakata, I. Nishida, *J. Less-Common Met.*, **162**, 39-49 (1990).
[6] I. Nishida, K. Masumoto, M. Okamoto, T. Kojima, *Trans. JIM*, **26**, 369-374 (1985).

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