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Studies on the formation of V_3Ga and V_3Si superconducting compounds by a new diffusion process

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In the present work, diffusion between vanadium and Cu-20 at.% Ga alloy and that between vanadium and Cu-20 at.% Si alloy were studied. An intermetallic compound, V_3Ga, is formed easily by the selective diffusion of gallium from the Cu-Ga alloy to the vanadium. V_5Si_3 and V_3Si are formed also by the selective diffusion of silicon from the Cu-Si alloy to the vanadium. Copper scarcely dissolves either in V_3Ga, V_5Si_3 or V_3Si. Copper is not effective for enhancing the formation of V_3Si unlike the case of V_3Ga. A large superconducting critical current density, J_c, is obtained in the V_3Ga formed at temperatures below 700°C while a much smaller J_c is obtained in the V_3Si formed at 800°C. Changes in J_c due to the heat-treatment can be interpreted by the grain growth of the compounds.

1. Introduction

Recently V_3Ga and V_3Si β-W type superconducting compounds have gained much interest because of their large current densities in high magnetic fields [1-3]. Such compounds show large current densities only when they are in a fine grained state. To obtain fine-grained V_3Ga, it is necessary to form it below 700°C above which the grain size of V_3Ga increases significantly [4]. The following two different processes have been reported for the formation of V_3Ga below 700°C [5].

Process A: Passing through a molten-gallium bath heated at 700°C, layers of VGa_2 V_3Ga_2 are formed on a vanadium substrate tape. Subsequently the tape is electroplated with copper and then heat-treated. The copper may be added to the molten-gallium bath instead of the plating. The copper much enhances the diffusion and enables the formation of V_3Ga below 700°C [6].

Process B: A composite of vanadium and Cu-Ga alloy is fabricated into a thin tape or wire by mechanical deformation. By subsequent heat-treatment at 650 to 700°C, gallium in the Cu-Ga alloy selectively diffuses into the vanadium and V_3Ga layers are formed. Copper does not dissolve in the V_3Ga layer and acts only as a "carrier metal" of the gallium. This newer process is more simple than process A [5].

In the present investigation, diffusion between vanadium and Cu-20 at. % Ga alloy in the specimen made by process B was studied in detail. Also diffusion between vanadium and Cu-20 at. % Si alloy was studied so as to know whether V_3Si compound can be formed by a process similar to that for making V_3Ga. V_3Si is more economical than V_3Ga because the price of silicon is much lower than that of gallium.

2. Experimental Methods

2.1. Specimen preparation

V-(Cu-Ga) diffusion specimens were made by rolling a composite of vanadium and Cu-Ga alloy containing 20 at. % of gallium. The composite was made by inserting a vanadium rod into a Cu-Ga alloy tube having an outer and inner diameter of 13 and 6 mm, respectively. The composite was rolled into a tape by grooved-rolling and flat-rolling. The thickness of the tape was 0.12 mm and the width of the tape was 6 mm, that of vanadium core being 3.7 mm.

V-(Cu-Si) diffusion specimens were made by dipping a vanadium substrate into a molten Cu-Si alloy bath containing 20 at. % of silicon.

The Cu-Si alloy was melted in a graphite crucible under an argon atmosphere. The Cu-Si alloy bath was held at 1100° C and a vanadium substrate, 0.1 mm thick and 3 mm wide, was immersed in the bath for 30 sec and pulled out through a thin slit made from silica.

V-(Cu-Ga) and V-(Cu-Si) diffusion specimens, 50 mm in length, were sealed in silica capsules under an argon atmosphere and heat-treated in a horizontal furnace followed by water-quenching.

2.2. Electron-probe microanalysis

The heat-treated specimens were cut into small pieces and the cross-section of the specimens was polished by a diamond paste. The thickness of the compound layers formed in the specimens was measured by an optical microscope. Diffusion reactions in the specimens were studied using an electron-probe X-ray microanalyser, type EMX-SM. The V$K\alpha$, Ga$K\alpha$, Si$K\alpha$ and Cu$K\alpha$ lines emitted from the specimens were used in the intensity counting while the Cu$L\alpha$ line was used in the line scanning instead of the Cu$K\alpha$ line. The correction for the absorption of X-rays in the specimens was made according to Thomas' procedure [7].

2.3. Critical current measurement

The critical current of the specimens was measured in magnetic field up to 70 kG at 4.2 K. Tapes 30 mm in length were cut from the heat-treated specimens and electroplated with a copper layer about 10 μm thickness. The tapes were connected to the copper terminals on the specimen holder by soft soldering. The magnetic field was generated by a 36 mm bore superconducting magnet made by Montgomery and one of the present authors (L.R.) [8]. The field was applied perpendicular to the length of the tape and parallel to the plane of the tape. The super-to-normal state transition was gradual and the current at which the voltage across the specimen exceeded 10^{-6} V was taken as the critical current I_c. The critical current density, J_c, was calculated by a formula, $J_c = I_c/dw$, where d was the thickness and w was the width of the superconducting compound layer, respectively.

3. Experimental Results

3.1. Results of the diffusion study

In Table I, compositions of the compounds formed in the specimens by various heat-treatments are summarized. The accuracy of the composition determination is of the order ± 2 at. % vanadium. In the V-(Cu-Ga) diffusion specimen only one compound is formed. Its composition is close to that of V_3Ga though it is a few per cent richer in vanadium than the stoichiometric composition. No other compound in the V-Ga system is formed. In the V-(Cu-Si) diffusion specimen, two compounds are formed of which compositions are close to V_5Si_3 and V_3Si, intermetallic compounds shown in the V-Si phase diagram [9]. The vanadium concentrations in both compounds are a few per cent poorer in vanadium than the stoichiometric compositions. Heat-treatment at a higher temperature or for a longer period causes a slight decrease of the gallium or silicon concentration in the compounds.

TABLE I Composition of the V-Ga and V-Si compounds formed in the V-(Cu-Ga) and V-(Cu-Si) diffusion specimens.

Specimen	Heat-treatment	Composition of compound (at. %)		
		V	Ga	Si
V-(Cu-Ga)	625° C × 100 h	76.7	23.0	
	700° C × 1 h	77.3	22.8	
	× 6 h	77.6	22.5	
	× 20 h	78.0	22.1	
	× 100 h	78.0	21.5	
	800° C × 1 h	78.0	22.6	
	× 6 h	77.8	21.8	
	× 20 h	78.5	21.4	
	× 100 h	78.3	21.7	
V-(Cu-Si)	800° C × 20 h	59.5		42.2
	× 100 h	59.8		42.0
	950° C × 1 h	58.7		42.5
	× 20 h	59.0		42.2
	× 50 h	72.2		29.4
		59.1		42.3
	× 100 h	72.5		28.8
		59.9		41.3
	1050° C × 50 h	73.2		27.0
		59.6		41.5

Relation between the thickness of the V_3Ga layer and the heating time at temperatures of 625, 700 and 800° C is shown in Fig. 1. On the abscissa the square root of the heating time is plotted. At the initial stage of the heat-treatment the thickness of the V_3Ga layer increases nearly proportionally to the square root of the heating time. The increase slows down after the heat-treatment for a long period. To obtain a 5 μm thick V_3Ga layer, heat-treatment for periods of

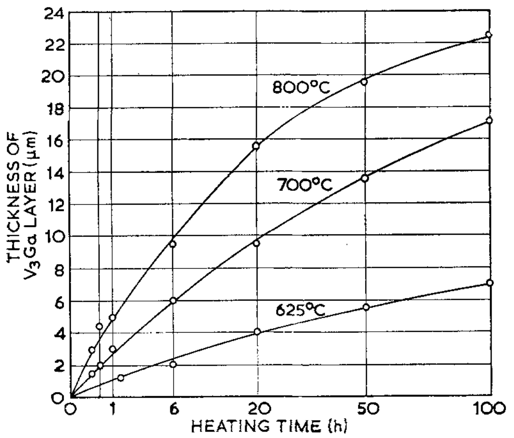

Figure 1 Thickness of the V_3Ga layer formed in the V-(Cu-Ga) diffusion specimen as a function of the heat-treatment time at quoted temperatures.

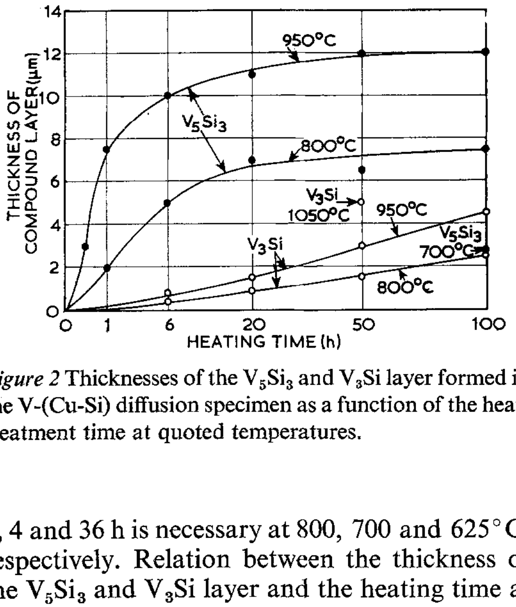

Figure 2 Thicknesses of the V_5Si_3 and V_3Si layer formed in the V-(Cu-Si) diffusion specimen as a function of the heat-treatment time at quoted temperatures.

1, 4 and 36 h is necessary at 800, 700 and 625° C, respectively. Relation between the thickness of the V_5Si_3 and V_3Si layer and the heating time at temperatures of 800 and 950° C is shown in Fig. 2. Results of the heat-treatment at 700° C for 100 h and at 1050° C for 50 h are also plotted. In the V-(Cu-Si) diffusion specimen, V_5Si_3 is formed predominantly. V_3Si is scarcely formed below 700° C.

A typical XMA line-scanning chart taken on the cross-section of the V-(Cu-Ga) diffusion specimen is shown in Fig. 3. The noticeable results on the chart are those where gallium selectively diffuses with vanadium resulting in the formation of V_3Ga layer in the specimen and copper scarcely dissolves into the V_3Ga layer. In the present XMA analysis, the minimum detectable amount of copper in V_3Ga, V_5Si_3 and V_3Si is about 0.2 at. %, respectively. The amount of copper dissolved in the V_3Ga is less than 0.3 at. % and nearly the same in the specimens heat-treated at 625, 700 and 800° C. The concentration gradient of the gallium in the Cu-Ga alloy layer heat-treated at 700° C is very small, less than 0.01 at. %/μm, indicating that the diffusion velocity of gallium in the Cu-Ga alloy is very large.

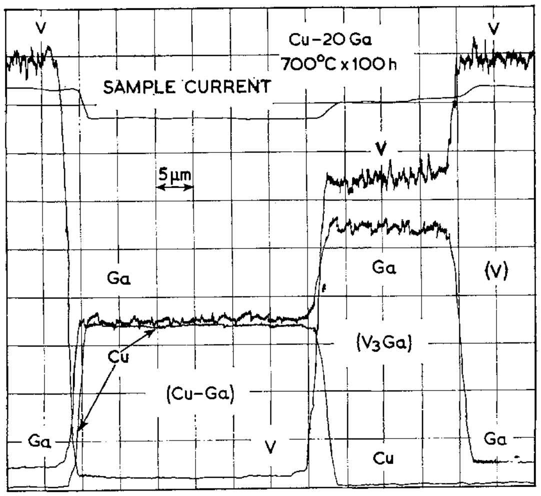

Figure 3 An XMA line-scanning chart taken on the cross-section of the V-(Cu-Ga) diffusion specimen heat-treated at 700° C for 100 h.

An XMA line-scanning chart taken on the cross-section of the V-(Cu-Si) diffusion specimen heat-treated at 950° C for 50 h is shown in Fig. 4. The formation of two compounds, V_5Si_3 and V_3Si, can be seen on the chart. The concentration gradient of the silicon in the Cu-Si alloy layer is very small, less than 0.01 at. %/μm, and the silicon selectively diffuses with vanadium, like the case of the diffusion in the V-(Cu-Ga) specimen. The amount of copper dissolved in the V_5Si_3 is less than 0.3 at. % and that dissolved in the V_3Si is less than 0.2 at. %.

In Figs. 5 and 6, electron absorption images taken on the cross-section of a V-(Cu-Ga) diffusion specimen and that taken on the cross-section of a V-(Cu-Si) diffusion specimen are shown. The Cu-Si layer side-diffusion boundary of the V-(Cu-Si) specimen heat-treated at 1050° C becomes very irregular, probably due to exceeding the melting point of the Cu-Si alloy at that temperature.

Decrease of the gallium concentration in the

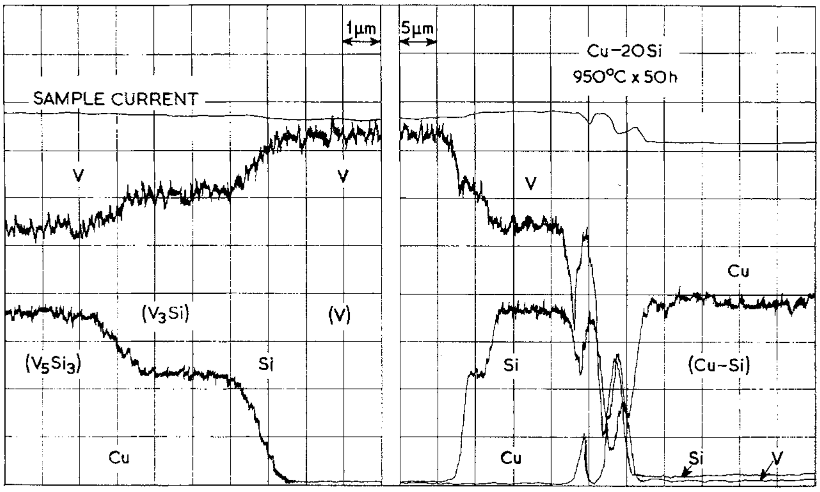

Figure 4 An XMA line-scanning chart taken on the cross-section of the V-(Cu-Si) diffusion specimen heat-treated at 950°C for 50 h.

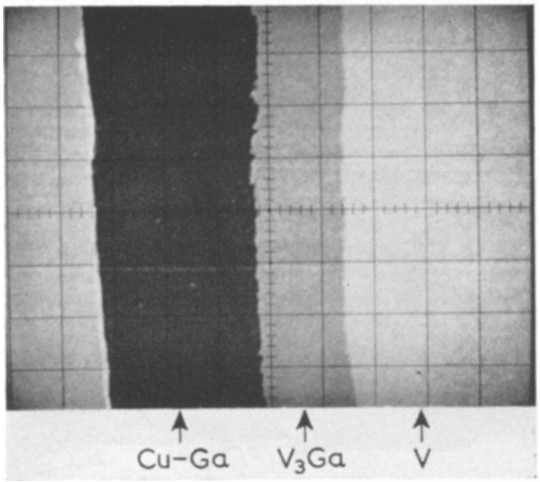

Figure 5 An electron absorption image taken on the cross-section of the V-(Cu-Ga) diffusion specimen heat-treated at 800°C for 20 h. Scale: 10 μm per division.

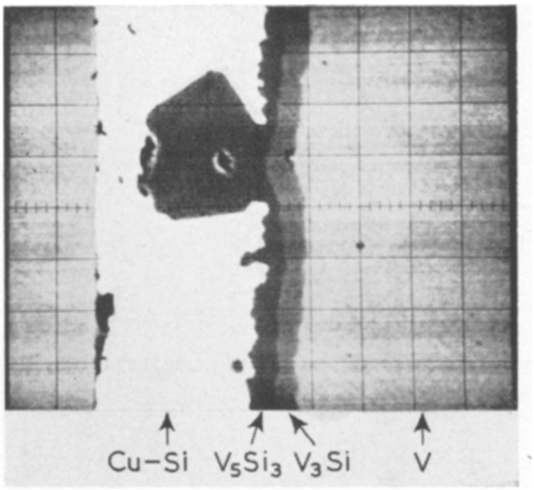

Figure 6 An electron absorption image taken on the cross-section of the V-(Cu-Si) diffusion specimen heat-treated at 1050°C for 50 h. Scale: 10 μm per division.

Cu-Ga alloy layer and that of the silicon concentration in the Cu-Si alloy layer with increasing heat-treatment time are shown in Fig. 7. The decrease of the gallium or silicon concentration causes the decrease of the thickness of the Cu-Ga or Cu-Si alloy layer, resulting in the increase of the copper concentration in the alloy layers. The decrease of the silicon concentration in the Cu-Si alloy layer is significant, due to the formation of V_5Si_3 layer which contains a large amount of silicon. The amount of decrease of gallium in the Cu-Ga alloy is in good agreement with the amount of gallium absorbed in the V_3Ga layer. A similar relation is found concerning the silicon concentration in the V-(Cu-Si) diffusion specimen.

3.2. Results of the critical current measurement

Pinning parameter, $\alpha = J_c \times H$, of the V_3Ga specimens in different heat-treatment conditions is shown as a function of the applied magnetic field, H, in Fig. 8. α versus H curves for the V_3Si specimens are shown in Fig. 9. α of the

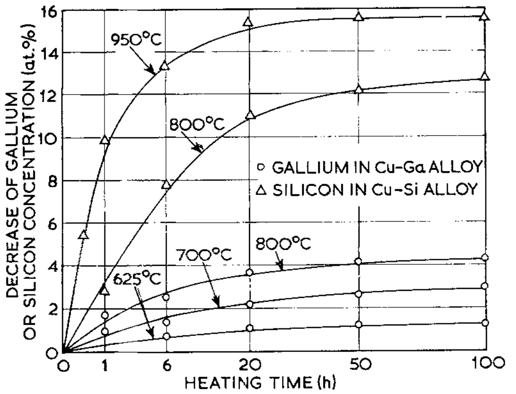

Figure 7 Decrease of the gallium concentration in the Cu-Ga alloy and that of the silicon concentration in the Cu-Si alloy as a function of the heat-treatment time at quoted temperatures.

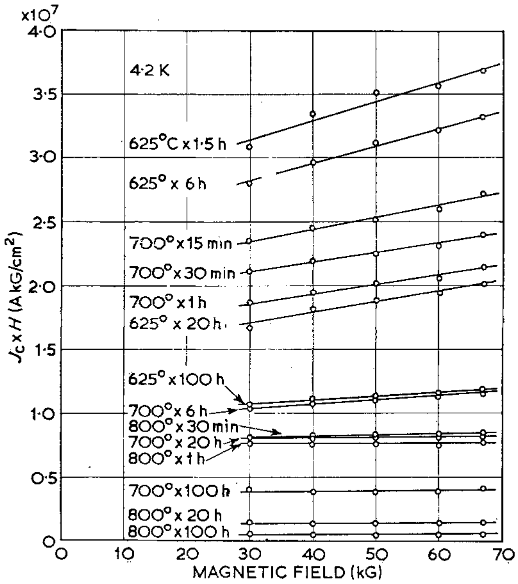

Figure 8 Pinning parameter of the V_3Ga specimen heat-treated in quoted conditions versus applied magnetic field.

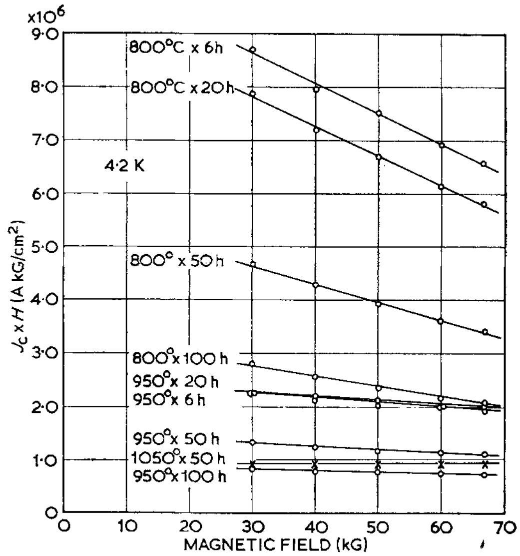

Figure 9 Pinning parameter of the V_3Si specimen heat-treated in quoted conditions versus applied magnetic field.

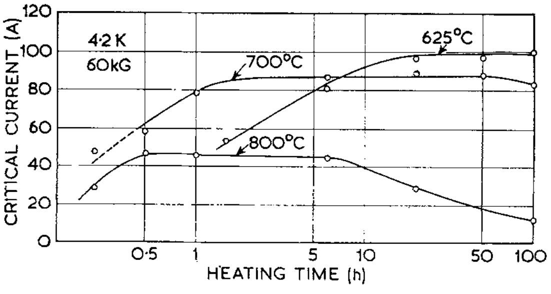

Figure 10 Critical current of the V_3Ga specimen as a function of the heat-treatment time at quoted temperatures.

V_3Si specimens heat-treated at 800°C is a little larger than that of the V_3Ga specimens heat-treated at the same temperature. Both in the V_3Ga and V_3Si specimens, larger α is obtained by a heat-treatment at a lower temperature and for a shorter period. The gradient of the α-H curves slightly differs as the heat-treatment conditions differ.

In Fig. 10, I_c of the V_3Ga specimens measured in a magnetic field of 60 kG is shown as a function of the heat-treatment time at temperatures of 625, 700 and 800°C. Nearly constant I_c is obtained when the heat-treatment time is between 2 and 50 h at 700°C and between 0.5 and 6 h at 800°C. At 625°C, I_c of the specimen reaches a constant value after the heat-treatment for 20 h. A similar plateau in I_c versus heat-treatment time curve also appears in the V_3Si specimens. I_c constant means that the J_c of the specimen is inversely proportional to the thickness of the compound layer, d. Such a relation is shown in Fig. 11. On the abscissa, the reciprocal value of d is plotted. J_c of the V_3Ga specimen is nearly proportional to $1/d$ when the d is not too small. For the same d, J_c of the specimen becomes smaller as the heat-treatment temperature becomes higher especially when the temperature exceeds 700°C.

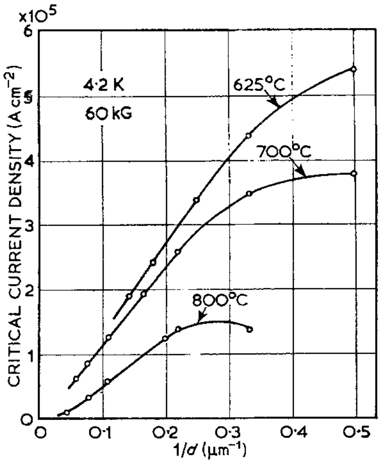

Figure 11 Critical current density versus reciprocal of the thickness of the V_3Ga layer formed at quoted temperatures.

4. Discussion

In the V-(Cu-Ga) and V-(Cu-Si) diffusion specimen, gallium and silicon selectively diffuse with vanadium and copper remains in the Cu-Ga and Cu-Si alloy layer. Only one compound, V_3Ga, is formed in the V-(Cu-Ga) specimen while two compounds, V_5Si_3 and V_3Si, are formed in the V-(Cu-Si) specimen. V_5Si_3 is formed predominantly by heat-treatments at 800 and 950° C. V_3Si is hardly formed by a heat-treatment below 700° C. The formation rate of the V_3Ga is about one order of magnitude larger than that of the V_3Si at 800° C. Copper scarcely dissolves either in V_3Ga, V_5Si_3 or V_3Si.

By the diffusion between gallium and vanadium at temperatures below 800° C, compounds richer in gallium, VGa_2 and V_3Ga_2, are predominantly formed. A very small amount of V_3Ga is formed by the diffusion between V_3Ga_2 and vanadium [10]. Copper dissolves both in VGa_2 and V_3Ga_2 as much as 7 and 4 at. %, respectively [6]. Without copper, diffusion between V_3Ga_2 and vanadium proceeds only through grain boundaries of V_3Ga_2. The copper addition changes the diffusion mode to a bulk one and then the V_3Ga can be formed easily below 800° C [6]. The enhancement of the diffusion due to the copper addition is caused by the decrease of the melting point of the V_3Ga_2 and the introduction of vacancies into the V_3Ga_2. In the present V-(Cu-Ga) diffusion specimen, there is plenty of copper. If VGa_2 or V_3Ga_2 were formed in the specimen, they might be immediately changed to V_3Ga by the effect of the copper. The copper scarcely dissolves in the V_3Ga and has no effect on the intrinsic superconducting properties of the V_3Ga.

In the V-(Cu-Si) diffusion specimen, two compounds, V_5Si_3 and V_3Si, are formed. As can be seen in Fig. 4, the copper scarcely dissolves in the V_5Si_3 and hence the copper cannot contribute to the enhancement of the formation of V_3Si, unlike the case of V_3Ga. That is the reason why V_3Si is not formed so easily as V_3Ga in the present diffusion specimens. If an element which is soluble in V_5Si_3 and not soluble in V_3Si could be found, it might be effective enhancing the formation of V_3Si.

The pinning parameter, α, of both V_3Ga and V_3Si specimens decreases with increasing heat-treatment temperature and period as shown in Figs. 8 and 9. This seems to be related to the grain growth of the compound by the heat-treatment. According to a transmission electron microscope study, the most important flux-pinning centres in a superconducting compound are grain boundaries and J_c is strongly related to the grain size [4]. J_c of the V_3Si formed at 800° C is about one order of magnitude smaller than that of the V_3Ga formed at 700° C. If V_3Si could be formed at a lower temperature, much higher J_c might be obtained.

I_c-constant heat-treatment time region is found in the V_3Ga specimen and J_c is inversely proportional to the thickness of the V_3Ga layer, d, as shown in Figs. 10 and 11. These results also can be interpreted by the grain growth of the V_3Ga. In a compound layer, a thin effective current-carrying layer consisting of finer grains seems to exist adjacent to the diffusion boundary. The remaining part of the layer consisting of coarser grains grown by the heat-treatment can scarcely contribute to the current carrying. The thickness of the effective current-carrying layer, d', might remain constant during the steady diffusion state and this makes I_c of the specimen constant. d' which corresponds to the thickness where the relation between J_c and $1/d$ deviates from the linearity in Fig. 11 is 3 to 4 μm.

When the heat-treatment time is too short, the thickness of the V_3Ga layer does not reach d' and I_c of the specimen is less than the constant value. When the heat-treatment time becomes too long the supply of gallium from the Cu-Ga alloy decreases. This makes the V_3Ga grain coarse and

d' small resulting in the decrease of I_c as shown in Fig. 10. For the same compound thickness, J_c decreases with increasing heat-treatment temperature as shown in Fig. 11. Decrease of J_c becomes significant above 700°C because the grain growth of V_3Ga becomes significant above this temperature. Comparing at a compound thickness, of 3µm J_c of the V_3Ga obtained in the present study is nearly the same as that of the V_3Ga obtained in process A [1]. Effects of the deviation from the stoichiometric composition in V_3Ga and V_3Si, shown in Table I, on J_c of these compounds are not yet clear.

5. Conclusions

(1) V_3Ga superconducting compound can easily be formed by the diffusion between vanadium and Cu-Ga alloy containing 20 at. % of gallium. No other compound in the V-Ga system is formed.

(2) V_5Si_3 and V_3Si compounds are formed by the diffusion between vanadium and Cu-Si alloy containing 20 at. % of silicon. V_5Si_3 is formed predominantly in the diffusion.

(3) Copper scarcely dissolves either in V_3Ga, V_5Si_3 or V_3Si. Copper is not effective in enhancing the formation of V_5Si unlike the case in the formation of V_3Ga.

(4) J_c of V_3Ga formed at 625°C is as high as 5×10^5 A/cm^2 in a magnetic field of 60 kG. J_c of V_3Si and V_3Ga formed at 800°C are about one order of magnitude smaller than this value.

(5) Changes in J_c of V_3Ga and V_3Si specimens due to heat-treatment can be interpreted by the grain growth of the compounds.

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