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Microstructure and superconductivity of V-based Laves-phase superconductor tape synthesized by a rapidly-heating/quenching process

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Abstract

The vanadium (V)-based Laves-phase compound is suitable for use as a high field superconductor for advanced fusion reactors because it shows radiation resistance and lower induced radioactivity in the fusion neutron irradiation condition compared with Nb-based A15 superconducting wires. We investigated the fabrication of $V_2(Hf,Zr)$ tapes by applying the rapidly-heating/quenching (RHQ) process. Pure Hf, Zr, and V powders were mixed and ball-milled, and then packed into pure Ta tubes. This powder-filled tube was cold-drawn and then flat-rolled into tapes of 0.2 mm in thickness. Precursor tape was set in the RHQ apparatus, then was continuously heated for 0.25 s and subsequently quenched into a liquid Ga bath. The highest temperature during the RHQ treatment was varied up to 2200 °C. Some specimens were additionally annealed in vacuum after the RHQ. We found a T_c value of about 8.88 K was obtained after the annealing.

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1. Introduction

Among the C15 type V-based Laves-phase compounds, $V_2(Hf,Zr)$ shows very attractive superconducting properties, with maximum critical transition temperature $T_c = 10.1$ K, maximum upper critical magnetic field H_{c2} above 20 T, and insensitivity to mechanical strain. In addition, V-based Laves-phase compounds show much higher radiation resistance than do Nb-based A15 compound wires and tapes [1].

In the R&D program of the ITER Engineering Design Activities (ITER-EDA), the neutron fluence and fast neutron flux on the superconducting magnet were estimated to be $4\text{–}20\times10^{23}$ n/m^2 and $2\text{–}10\times10^{16}$ n/m^2 s, respectively [2]. The superconducting magnet in a practical nuclear fusion reactor is assumed to be severely affected by the radiation. The decay of induced radioactivity to a hands free level on the V-based Laves-phase compound requires about 10 years, but that of the Nb-based A15 phase compound exceeds 10000 years [3]. Therefore the V-based Laves-phase compound is superior to Nb-based A15 phase compounds, and promising as the high field conductor for the advanced fusion reactor.

Inoue et al. have fabricated $V_2(Hf,Zr)$ multi-filamentary wires by a diffusion process between V–Hf alloy and Hf–Zr alloy, and reported that a rather high temperature of 1000 °C was required for heat-treatment in order to obtain a high critical current density (J_c) in the high magnetic field [4]. However, the overall J_c of those multifilamentary wires was relatively low, because many 2nd phases (Zr–Hf based bcc phase) were also formed with the Laves-phase. It appears that a new process which does not pass through the diffusion reaction is required to fabricate $V_2(Hf,Zr)$ wires having a higher J_c

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value. We tried to fabricate the V_2(Hf, Zr) Laves-phase compound tapes by applying the rapidly-heating and quenching (RHQ) process to the powder-in-tube processed precursors. The RHQ process has been successfully used to develop advanced Nb_3Al conductors and is very interesting as a high-temperature, short-time heat-treatment on precursors wires [5]. We investigated the microstructures and superconducting properties of the samples fabricated by RHQ process for this paper.

2. Experimental procedure

In this study, mono-cored Laves-phase compound precursor tapes were fabricated through the conventional powder-in-tube (PIT) method. At first, high purity metal vanadium (V), hafnium (Hf), zirconium (Zr) powders and a tantalum (Ta) tube having 10 mm of inner diameter, 20 mm of outer diameter and 50 mm of length were prepared. The nominal atomic composition of these metal powders was adjusted to be $V_2(Hf_{0.5},Zr_{0.5})$. This mixed powder was well ground by hand, and then wet ball-mill processing was carried out for 3 h to homogenise the mixed metal powder. In the ball-mill processing, mixed powder was set into zirconia (ZrO_2) pots with some ZrO_2 balls and then they were saturated with the ethyl alcohol to prevent contamination by the air. After ball-mill processing, the mixed powder was packed into Ta tubes. These composites were cold-rolled with a grooved and flat roller to tapes of about 0.2 mm thickness. The precursor tapes were set into the RHQ apparatus, and the RHQ treatment was applied in a dynamic vacuum chamber. The precursor tapes, moving at 0.4 m/s of velocity, were continuously heated up to the desired temperatures by resistive-heating during 0.25 s, with a dc current transported between an electrode pulley and a molten metal Ga bath. Subsequently, the tapes were continuously quenched into the Ga bath at about 40 °C from 2200 °C. The coated Ga on the tapes was removed by chemical etching in hydrochloric acid after the RHQ treatment. Then, part of as-quenched tapes were additionally annealed at temperatures between 500 and 700 °C for 20 h in the vacuum. The fabrication process of precursor tape in this study and a schematic illustration of the RHQ apparatus are shown in Fig. 1.

T_c values of the as-quenched and annealed samples were measured by a dc four-probe resistive method. Cu plating was added to the sample in order to reduce the contact resistance for the measurement. By using Cu K_α radiation, we measured the X-ray diffraction (XRD) patterns for the as-quenched and post-annealed samples to determine the crystal structures of the phases formed in the tape. Microstructures of transversely polished cross-sections of the samples were observed in detail by using a scanning electron microscope (SEM). Phase identification, mapping of composite element and quantitative composition analysis of crystal grains were carried out using an energy dispersive X-ray (EDX) spectrometer.

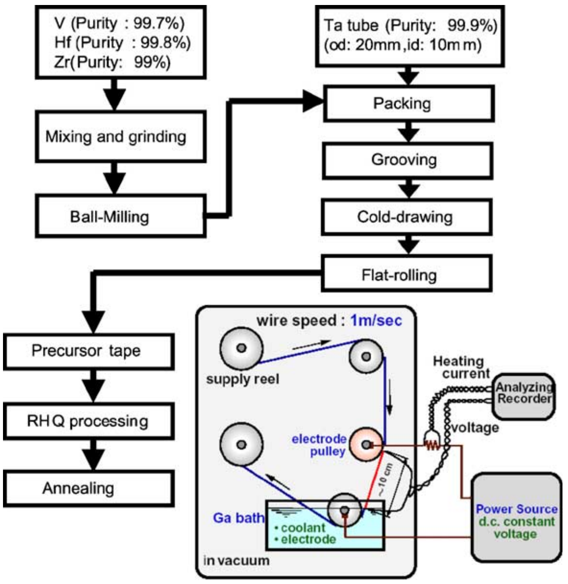

Fig. 1. The fabrication process of precursor tape in this study and the schematic illustration of the RHQ apparatus.

3. Results and discussion

3.1. Microstructure and T_c property of the as-quenched sample through RHQ process

The XRD patterns of the samples that received the RHQ processing are shown in Fig. 2. The diffraction peaks used in the measurement are Cu K_α lines. The values shown in Fig. 2 are the heating energy density, which the energy supplied to the precursor tape during RHQ processing from a dc powder supply. The larger energy density means a higher temperature was achieved during RHQ processing. When the value of heating energy density was about 2.19 J/mm^3 (1100 °C), Laves-(C15) and β-phases were formed directly by the diffusion reaction. Because the peak width of the C15 phase was relatively wide, the crystal structure of formed C15 phase seems to be disturbed. As the heating energy density increased larger than 2.19 J/mm^3, the peaks of the C15 phase disappeared, and the as-quenched core became β-phase and an amorphous phase. It is noteworthy that the HfO_2 peak appears for temperatures over 1500 °C and is sharpened with increasing temperature. The reason is that the melting point of metal Hf is the highest of the elements and the Hf did not melt and

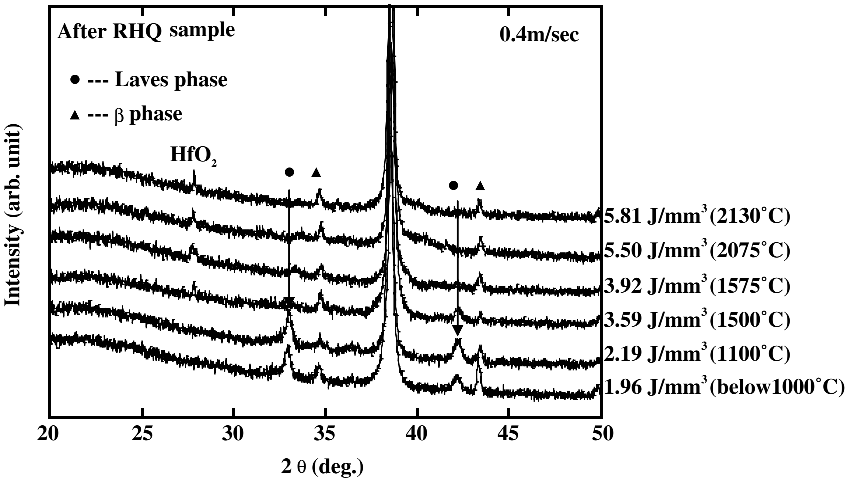

Fig. 2. The XRD patterns of the as-quenched samples after RHQ processing.

some remained following the lower temperatures of RHQ processing. Then the remaining metal Hf reacted with the air in the Ta sheath at high temperatures. We measured the distribution of metal elements on the cross-sectional and surface area of the as-quenched samples in order to identify the crystal phases that formed. Fig. 3 shows the typical distribution of V element in the cross-sectional area of the as-quenched samples. Fig. 3(a)–(d) are samples heated by 1.96, 3.59, 3.92 and 5.81 J/mm^3, respectively. In the case of the sample at 1.96 J/mm^3, we found that there is gradation and segregation of metal V. According to the EDX analysis, we confirmed that C15 and β-phases were formed around the segregation of metal V, and then nonreacted metal V, Hf and Zr remained. It was reported that β-phase formed as a secondary phase to the diffusion reaction to form C15 phase, and it was the Hf–Zr bcc alloy which dissolved metal V from 15 to 25 at.% [6]. The segregation of the metal V disappeared with increasing temperature when the heating energy density reached 3.92 J/mm^3. In the case of the sample at 5.81 J/mm^3, we found that distribution of the V metal had become almost homogeneous and the homogeneous region was an amorphous phase based on SEM–EDX analysis. Although the tendency observed in the cross-sectional structure was similarly observed in the surface structure, concentrations of Hf and β-phase were confirmed in the surface structure following high

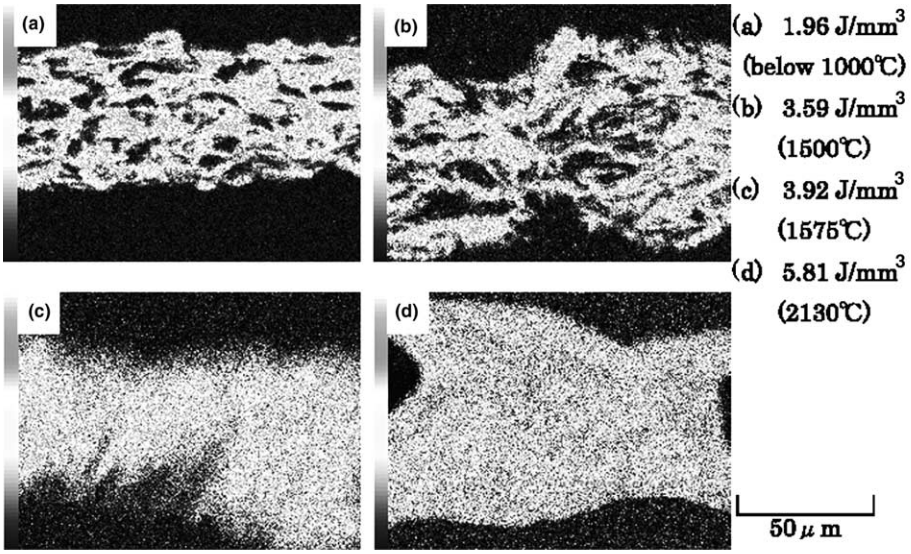

Fig. 3. The typical distribution of V element in the cross-sectional area of as-quenched samples after RHQ processing.

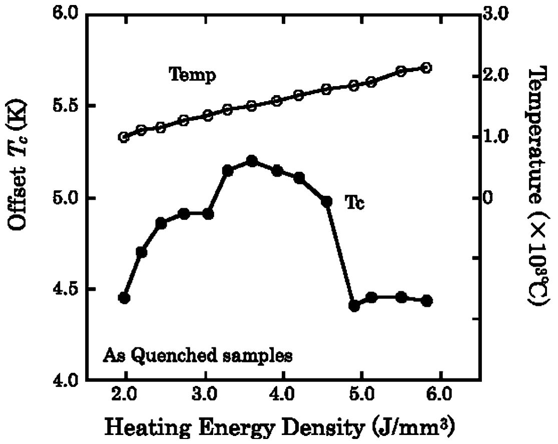

Fig. 4. The relationship between offset T_c, temperature during RHQ processing and heating energy density on the as-quenched samples with tape velocity of 0.4 m/s.

temperature RHQ processing. The results of EDX analysis of cross-sectional and surface regions of the tape core were consistent with the results of XRD. The formation of HfO_2 was caused by oxidization of the concentrated metal Hf.

In order to evaluate the superconducting property of as-quenched samples, we measured the T_c value of several as-quenched samples. Fig. 4 shows that the relationship between offset T_c, the temperature reached during RHQ processing and heating energy density on the as-quenched samples with tape velocities of 0.4 m/s. Offset T_c values of all the as-quenched samples were estimated to be below 5.50 K, but they were improved with increasing heating energy density. The maximum offset T_c value of 5.20 K was obtained when the heating energy density was about 3.59 J/mm³. These T_c values of as-quenched samples were remarkably lower than that of stoichiometric V_2(Hf,Zr) Lave phase, and they were an indication of T_c values of the forming β-phase. The T_c value of V_2(Hf,Zr) amorphous phase is below 4.2 K.

3.2. Effect of post-annealing on the T_c property of the sample through RHQ process

We confirmed that as-quenched samples after RHQ processing had an amorphous phase from the results of Figs. 2–4. Annealing in vacuum was used to attempt to crystallize C15 phase from the amorphous phase. Fig. 5 shows the relationship between offset T_c and heating energy density on the annealed samples. The annealing conditions are 500, 600 and 700 °C for 20 h in the vacuum. We found that the offset T_c values of annealed samples were improved with increasing annealing temperature, and an optimum annealing temperature was 700 °C in this study. The maximum offset T_c value was obtained 8.88 K when the heating energy density was about 3.59 J/mm³ on the sample annealed at 700 °C. The heating energy density leading to the maximum offset T_c value was shifted to the higher energy compared with that of as-quenched sample. The heating energy density of 3.59 J/mm³ was the threshold energy for the formation of the amorphous phase by the RHQ processing from the results of XRD and SEM–EDX. This suggests that the crystallization of C15 phase from the amorphous phase is effective for obtaining a high T_c value. In contrast, offset T_c values of annealed samples between 1.96 and 3.59 J/mm³ were decreased in comparison with those of as-quenched samples. This suggests that the C15 phase was not formed and β-phase was mainly formed from the quenched structure of low heating energy density even if the annealing at 700 °C was carried out. Offset T_c values of annealed samples of over 3.59 J/mm³ were drastically improved compared with those of as-quenched samples. In this case the crystal structure of the annealed sample was mainly C15 phase, and it formed from amorphous phase that formed during RHQ processing at high heating energy density. Furthermore, we found that offset T_c values of the annealed samples at 5.81 J/mm³ were lower compared with those at 3.59 J/mm³. This is because the Hf concentration in the C15 phase that formed from the amorphous phase decreased with increasing heat energy density as the metal Hf was converted to HfO_2. The presence of HfO_2 remaining was shown from results of XRD and SEM–EDX in Figs. 2 and 3. It was known that the T_c value of V_2(Hf,Zr) was decreased with decreasing of Hf concentration in Laves-phase [7]. This suggests that T_c values of

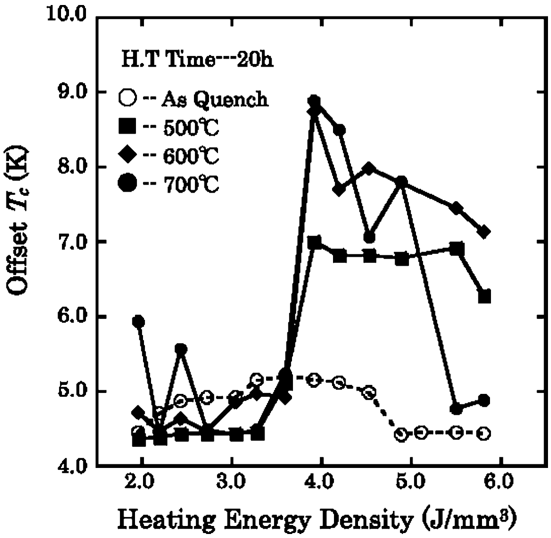

Fig. 5. The relationship between offset T_c and heating energy density on the post-annealed samples with tape velocity of 0.4 m/s.

the annealed samples are mainly determined by the phases in the as-quenched wire.

4. Conclusions

We succeeded in fabricating C15 compound superconductor tape by applying the RHQ process to the powder-in-tube processed precursors. A homogenous amorphous phase forms in the core of the precursor tape when a heat energy density over 3.5 J/mm^3 of RHQ process is applied. We found that the C15 phase having a high offset T_c value was transformed from the amorphous phase during annealing. The maximum offset T_c value was obtained 8.88 K.

Acknowledgements

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