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Fabrication of V-Based Laves Phase Compound Multifilamentary Wires by Applying a Rapidly-Heating/Quenching Process to PIT Precursors and Using a V Tube

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Abstract—We fabricated V-based Laves phase compound such as $V_2(\text{Hf}, \text{Zr})$ multifilamentary wire by applying a rapidly-heating/quenching (RHQ) process. Pure Hf and Zr metal powders were mixed and it put in high pure V tube composed with tantalum (Ta), and it was drawn in order to make wire (powder-in-tube (PIT) method). The wires were heat-treated by RHQ process, and some were annealed additionally in vacuum. Since Ta has a higher melting point than V, it is expected that the alloying prevents from breakage of the precursor wire during RHQ treatment because the maximum temperature exceeds 2500 K. SEM observation confirmed that the thick reaction layer within about 10 microns was formed on the boundary of the powder mixture filament and the V matrix after the RHQ. T_c values of the as-quenched samples increased with increasing maximum temperature during RHQ process, and the maximum mid point T_c value was about 8.0 K. The transport J_c properties under magnetic fields were also investigated.

Index Terms—Multifilamentary wire, RHQ process, superconducting properties, V-based Laves (C15) phase.

I. INTRODUCTION

IN the ITER project, nuclear burning plasma experiments between Deuterium (D) and Tritium (T) reaction are planned for the demonstration of future advanced fusion reactors. Generally, a fusion reactor requires high magnetic field to confine the D-T plasma and maintain the fusion reaction. Especially, it is anticipated that the generation of 14 MeV neutrons by the D-T reaction increases in advanced reactors requiring higher efficiency than ITER. Therefore, neutronic properties of superconducting materials are required as well as high magnetic field properties

in order to realize an advanced fusion reactor. It is well known that half-life of niobium (Nb) by nuclear transition from ^{93}Nb to ^{94}Nb is estimated to be 2.0×10^4 years. The decay period of induced radioactive isotopes to a hands-on level for Nb-based A15 phase compound was evaluated to be about ten thousand years because of a long half-life of Nb [1]. On the other hand, the attenuation of induced radioactivity to the hands on level for V-based Laves phase compound is about ten years [1]. In the case of advanced fusion reactors such as “DEMO” and commercial fusion plants, the superconducting magnet can be assumed to be severely irradiated by neutron irradiation. Neutron irradiation has been modeled for ITER using monte-carlo simulation [2]. Therefore the V-based Laves phase compound is superior for neutronics properties compared with those of Nb-based A15 phase compounds.

Since the discovery of superconductivity in the C15 type V-based Laves phase compound $V_2\text{Zr}$ by Matthias *et al.* [3], it is clear that its superconducting properties are improved by the addition of various elements, especially Nb and Ta and Cr [4]. Among the C15 type V-based Laves phase compounds, $V_2(\text{Hf}, \text{Zr})$, show very attractive superconducting properties a maximum $T_c = 10.1$ K, maximum H_{c2} above 20 T and a insensitivity to mechanical strain. We thought that C15 Laves phase compound superconductors were promising as low activation and high field conductors for advanced fusion reactors.

One of the authors, K. Inoue *et al.*, has fabricated $V_2(\text{Hf}, \text{Zr})$ multi-filamentary wires by the diffusion process between V-Hf alloy and Hf-Zr alloy, and reported that a rather high temperature of 1300 K was required for heat-treatment in order to obtain the high critical current density (J_c) in the high magnetic field [5]. However, the overall J_c of those multifilamentary wires was relatively low, because a lot of 2nd phases (Zr-Hf based bcc phase) were also formed along the Laves phase. So, we thought that it needed a new process which does not pass through the diffusion reaction in order to fabricate $V_2(\text{Hf}, \text{Zr})$ wires with higher J_c values. We tried and succeeded to fabricate the $V_2(\text{Hf}, \text{Zr})$ Laves phase compound tapes by applying the RHQ process to the powder-in-tube processed $V_2(\text{Hf}, \text{Zr})/\text{Ta}$ composite precursors [6]. The RHQ process has been successfully developed for advanced Nb_3Al conductors and is very interesting as a high-temperature short-time heat-treatment on

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precursor wires. In this study, we fabricated the Laves phase compound multifilamentary wire synthesized Hf-Zr metal powder mixture/V tube composite and its microstructures and superconducting properties were investigated.

II. PROCEDURE FOR V-BASED LAVES PHASE COMPOUND MULTIFILAMENTARY WIRE

In this study, the multifilamentary Laves phase compound precursor wire was fabricated through the conventional Powder-In Tube (PIT) method. Firstly, high purity metal hafnium (Hf) and zirconium (Zr) powders and vanadium (V) tube having a 10 mm inner diameter and a 20 mm outer diameter and 50 mm in length were prepared, respectively. The metal Hf and Zr powders were adjusted to have equal molar ratio. This powder was well ground by hand, and then wet ball-mill processing was carried out for 3 hours to homogenize the mixed metal powder. In the ball-mill processing, mixed powder was put into zirconia (ZrO_2) pots with some ZrO_2 balls and they were satisfied by the ethyl alcohol to prevent the oxidation of these powder by contamination of the air. After the ball-mill processing, mixed powder was packed into V tubes. This composite ((Hf,Zr)/V) was cold-rolled with a grooved roller and the wire drawn a diameter of about 1.20 mm. Intermediate annealing was carried out several times at 1173 K for 1 hour to soften this composite during this deformation. The (Hf,Zr)/V composite was cut into short pieces, and they were stacked into a tantalum (Ta) tube having 14 mm of inner diameter, 20 mm of outer diameter and 50 mm of length. The number of stacked (Hf,Zr)/V composite was 55 pieces. This composite ((Hf,Zr)/V/Ta) was cold-rolled with a grooved roller and drawing machine to wire of about 0.754 mm diameter as well as (Hf,Zr)/V composite.

The precursor wire was set into RHQ apparatus, and it was applied to the RHQ treatment in a dynamic vacuum chamber. The precursor wire was continuously heated up to the several purpose temperatures with moving at 1.0 m/sec of velocity. The precursor wire was heat treated by resistive-heating during 0.1 sec, and a dc current transported between an electrode pulley and a molten metal Ga bath. Subsequently, the wire was continuously quenched into the Ga bath at about 320 K from above 2500 K. The coated Ga on the wires was removed by chemical etching in hydrochloric acid after the RHQ treatment. Then, some of the as-RHQ wires were additionally post-annealed at several temperatures for 10 hours in the vacuum. A schematic illustration of the fabrication process for the precursor wire in this study is shown in Fig. 1.

T_c and I_c values of the as-RHQ and post-annealed samples were measured by dc four-probe resistive method. And then, I_c measurement was carried out under the several magnetic fields up to 15 T at 4.2 K. The J_c values of these samples were calculated from I_c value and cross-sectional reaction area. The samples were Cu plated in order to reduce the contact resistance for the I_c 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 wire. The microstructures of transversely polished cross-sections of the samples were observed

Fig. 1. The schematic illustration of fabrication process on precursor wire.

Fig. 2. Typical SEM photograph of the cross-sectional structure on the prepared (Hf, Zr)/V/Ta 55 cored multifilamentary wire.

using a Scanning Electron Microscope (SEM). Phase identification, mapping of composite elements and quantitative composition analysis of crystal grains were carried out by using an energy dispersive X-ray (EDX) spectrometer.

III. RESULTS AND DISCUSSIONS

A. Microstructure of the As-Quenched Sample Through RHQ Process

Fig. 2 shows a typical SEM photograph of the cross-sectional structure of the prepared (Hf, Zr)/V/Ta 55 cored multifilamentary wire. We succeeded in long length deformation of multifilamentary wire having 0.754 mm diameter by carrying out the intermediate annealing in vacuum several times. In this photograph, gray and black area indicates metal Ta sheath and metal V matrix. Many Hf-Zr mixed powder filaments have a place in V matrix. The average diameter of the Hf-Zr mixed powder filaments was about 30 microns.

The XRD patterns of the samples subjected to the RHQ processing are shown in Fig. 3. The values shown in Fig. 3 are indicated heating energy density; the energy is supplied to the precursor wire during RHQ processing from a dc powder supply. A larger energy density means a higher heating temperature during RHQ processing. We confirmed that C15 and β phases were formed directly by the diffusion reaction at every energy density. It was reported [4], [7] that β phase formed as the secondary phase through the diffusion reaction to form C15 phase, and it was the Hf-Zr bcc alloy which dissolved metal

Fig. 3. Typical XRD pattern of the as quenched samples applying several RHQ conditions.

Fig. 4. Typical SEM photograph of the cross-sectional structure on the as quenched samples. Fig. 4 a), b), c) and d) are the 3.07, 4.74, 5.58 and 6.52 J/mm³ samples.

V from 15 at% to 25 at% [6]. We found that C15 phase and β phase are able to form between Hf-Zr powder filament and V matrix by high-temperature and short-time diffusion reaction. The peak width of the C15 phase was relatively wide, the crystal structure of formed C15 phase seems to be disturbed. The other hand, peak of metal Hf appears every samples and intensity of this peak lowered with increasing of heating temperature. This is why that the melting point of metal Hf is the highest all the composite elements, and the metal Hf sufficiently did not melt and remained partially in the powder mixture filaments on the RHQ processing.

Fig. 4 shows typical SEM photographs of the as-quenched samples. Fig. 4(a), (b), (c) and (d) are the samples of 3.07, 4.74, 5.58 and 6.52 J/mm³, respectively. In the case of the 3.07 J/mm³ sample, no reacted metal Hf and Zr powders were

Fig. 5. The relationship between offset T_c value and heating energy density on the as-quenched and post-annealed samples.

observed by EDX analysis in the filaments. The heating temperature was lower than the melting point of the Hf-Zr mixture powder. In the cases of the samples above 4.74 J/mm³, a thick reaction layer was formed on the boundary of powder mixture filament and V matrix after the RHQ treatment and subsequently the reaction layer expanded with increasing heating energy. According to the EDX analysis, we confirmed that C15 and β phases were formed in the reaction layer, and that non-reacted metal Hf and Zr remained in the filament. For the 6.52 J/mm³ sample, dendrite structure was formed around the filaments. We found that Hf and Zr were sufficiently melted for the 6.52 J/mm³ sample, and the melted liquid was supercooled by quenching.

B. Superconducting Properties of Laves Phase Compound Multifilamentary Wire Through RHQ Process

Fig. 5 shows the relationship between offset T_c and heating energy density on the as-quenched and post-annealed samples. The post-annealing conditions were 773 K, 873 K, 973 K, 1073 K and 1173 K for 10 hours. Offset T_c values of low energy heating samples were estimated below 5.50 K, its value corresponded to T_c value of metal V and Ta. By an accompanying increase of heating energy density, offset T_c values of as-quenched and post-annealed samples were drastically improved from 4.0 J/mm³, and they were decreased for heating energy densities over 6.0 J/mm³. It suggests that this tendency was consistent with microstructures of the samples shown to Fig. 4 and T_c value corresponds to volume fraction of Laves phase. Maximum offset T_c value was about 8.22 K. This value is lower than that of stoichiometric Laves phase (10.1 K). This may be because the composition of our Laves phase is inhomogeneous locally since the composite filament is prepared by a powder mixture. It was also observed that there was no increase the difference between the offset T_c and heating energy densities with post-annealing temperature. We think that the T_c of

Fig. 6. $J_c - B$ curves of the as-quenched and post-annealed samples of 5.86 J/mm^3 .

the Laves phase did not depend on crystallization of the Laves phase. We measured I_c values of as-quenched and post-annealed samples under the several magnetic fields at 4.2 K in order to evaluate the J_c properties. The typical $J_c - B$ curves of the as quenched and post-annealed samples of 5.86 J/mm^3 are shown to Fig. 6. The RHQ heating energy density of these samples was 5.86 J/mm^3 . The post-annealing conditions are 773 K, 873 K, 973 K and 1173 K for 10 hours. The maximum J_c value was estimated to be 1300 A/mm^2 at 4.2 K and 1 T, for a sample that was post-annealed at 873 K. This value was the J_c value of the reaction layer produced through RHQ because the H_c value of the V matrix and Ta sheath was below 1 T. J_c dependence of magnetic field on the sample post-annealed at 873 K was higher than for the as-quenched sample, and the H_{c2} value of the sample post-annealed at 873 K was also improved compared to the as-quenched sample. On the other hand, the J_c dependence on magnetic field for the sample post-annealed at 1173 K was lower than for the as-quenched sample as well as its H_{c2} value. We found that optimum post-annealing temperature in this study was lower than that of temperature on the diffusion samples. Generally, there was eutectic transformation temperature at 1050 K between Laves phase and metal Zr in V-Zr system equilibrium diagram. And we thought that Laves

phase which was formed by RHQ treatment will be unstable state in this study. It is known that the minimum diffusion formation temperature of β phase (secondary phase) for the V_2Zr Laves phase is about 1073 K [7]. We believed that the effect of post-annealing was only to reduce the thermal strain by RHQ, and the optimum post-annealing condition was a lower temperature without phase transformation of the Laves phase.

IV. CONCLUSION

We have successfully fabricated V-based Laves phase compound $\text{V}_2(\text{Hf}, \text{Zr})$ multifilamentary wire by applying a rapidly-heating/quenching process to PIT precursor. The results of XRD and SEM indicated that the Laves phase was formed by only the RHQ treatment, and that the volume fraction and reaction thickness of the Laves phase were increased by increasing the heating energy density. The J_c value of Laves phase was improved by low post-annealing temperature without phase transformation of Laves phase.

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