MULTIFILAMENTARY Nb_3Sn WIRES REACTED IN HYDROGEN GAS

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ABSTRACT

Reaction of Nb_3Sn wires in an Incoloy 908® conduit in the presence of oxygen can decrease the conduit's fracture toughness. This may be avoided by reacting in a reducing atmosphere of 5% hydrogen-95% argon. The effects of the hydrogen reaction on the superconductive properties of bronze-process and internal-tin-process Nb_3Sn wires were investigated. Compared with the standard heat treatment in partial vacuum, critical currents decreased in the bronze wire by 12% at 12 T and 14% at 5 T, and in the internal-tin wire by 4% at 12 T and 10% at 8 T. Hysteresis losses over a ±3 T field cycle were reduced by 14% for the bronze wire and by 8% for the internal-tin wire by the hydrogen heat treatment, approximately proportional to the reduction in critical current. The critical temperature was reduced by 0.5 K. There was no significant effect on the residual resistivity ratio of the stabilizing copper.

INTRODUCTION

Niobium-tin superconducting cables for the International Thermonuclear Experimental Reactor (ITER) central solenoid model coils were jacketed in Incoloy 908® alloy conduits. The fabrication and heat treatment of the coils required excellent control of the atmospheric environment, since Incoloy 908® is susceptible to stress-accelerated grain-boundary oxidation (SAGBO) at temperatures above 540 °C and tensile stresses exceeding 200 MPa. Heat treatments of the model coils were performed with care in an inert gas atmosphere [1]. Levels of contaminants such as lubricants, oxygen (< 0.1 ppm) and moisture (< 1 ppm) had to be

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carefully checked at around 460 °C prior to entering the SAGBO temperature regime. One possible way to prevent SAGBO and to make heat-treatments easier is to use a hydrogen-gettered gas during heat treatment. The hydrogen can reduce the oxygen potential to the point where SAGBO does not occur. Hydrogen is used routinely in the processing of Incoloy 908® in the mill to prevent oxidation during annealing between rolling reductions and to bright-anneal the final product.

This paper describes experimental results of a study to determine the effects on the superconductive properties of Nb_3Sn wires when the reaction is carried out in a 5% hydrogen-95% argon gas atmosphere.

EXPERIMENTAL METHODS

Two types of ITER Nb_3Sn wires were used in this study. Strand A was a Vacuumschmelze (VAC) bronze-process wire with a Ta diffusion barrier under the copper stabilizer (sample 54.4). Strand B was an Intermagnetics General (IGC) internal-tin wire with a diffusion barrier composed of thin Nb and Ta layers under the stabilizer (sample B6770-1). Filament alloys of both strands were Nb-7.5% Ta (by mass). Both wires were about 0.81 mm in diameter and had a twist pitch of 0.9 cm. They were Cr plated on the surface, but specimens for critical current measurement had the Cr plating removed by chemical etching before reaction for convenience in soldering. Prior tests assured that Cr plating had no effect on the critical current of samples reacted in hydrogen gas.

The test specimens were heat treated using the following schedule: ramp up at 6 °C/h to 460 °C and hold for 144 h, ramp up at 6 °C/h to 570 °C and hold for 220 h, ramp up at 6 °C/h to 650 °C and hold for 175 h, and ramp down at 25 °C/h to room temperature.

Critical current, hysteresis loss, and other test samples of Nb_3Sn strands were reacted in a gas flow of "Grade 5," 5% hydrogen-95% argon. This gas is not flammable and is commonly used in industry. Control samples were heat-treated in a gas flow of pure argon. Test specimens for measurements of critical current (I_c) and hysteresis loss were fabricated in the same manner used for the ITER second benchmark test [2]. The sample holder for I_c measurement was a 32 mm diameter Ti-6Al-4V alloy barrel with copper current rings. The conventional Ti-6Al-4V alloy sample holder could not be used in hydrogen gas because of hydrogen reaction with the Ti alloy (Ti hydride). Barrels for the heat treatment of samples for critical current measurement were made of Incoloy 908® with exactly the same dimensions as the Ti-6Al-4V barrel. Since Incoloy 908® is magnetic, and would therefore add to the applied field [3], the test specimen was transferred from the Incoloy barrel to a Ti-6Al-4V alloy barrel. Samples were soldered to the end posts in such a way that the thermal contraction of the wire was constrained by the lower thermal contraction coefficients of the Ti-6Al-4V barrels. The effect of these constraints was to place tension on the Nb_3Sn wire. The critical currents were measured at 4.2 K with a voltage-tap separation of 0.5 m and a criterion of 10 μV/m. The n-values of the V-I curves were evaluated in the electric field range 10 to 100 μV/m.

Wires for measurement of hysteresis loss were wound and heat treated on an oxidized stainless steel threaded rod (diameter 6.5 mm, pitch 1 mm). Specimens of about 7 turns were cut carefully from the reacted coils. Each specimen was over 10 twist pitches in length [4]. Hysteresis loss was measured for a full cycle of +3 T to -3 T to +3 T with a magnetometer based on a superconducting quantum interference device (SQUID). The field was applied along the axis of the coil, approximately transverse to the wire. Residual resistivity ratio (RRR) was measured as the ratio of resistances at 273 K and 20 K using a four-probe measurement and a voltage tap separation of approximately 30 mm.

Additional magnetization measurements were made in fields up to 14 T using a vibrating-sample magnetometer (VSM). The samples for the VSM measurements were straight wires, about 5 mm long, situated perpendicular to the applied field. The field was swept continuously at 3.3 mT/s for the measurement, thus applying an electric field of about 17μV/m. Measurements were made at 4.2 K and at 12 K; at 12 K the upper critical field B_{c2} could be exceeded by the available field. Specific heat measurements were made using a physical property measurement system (PPMS) on very small samples (~0.5 mm long) in a relaxation calorimeter. Both sample sets were in a state of zero net wire stress, which means a state of precompression on the Nb_3Sn filaments. Thus, compared to the critical-current measurements made on the Ti-6Al-4V barrels, the Nb_3Sn is expected to have reduced critical temperature T_c, critical-current density J_c, irreversibility field B^*, and upper critical field B_{c2}. The strands were examined for microstructural variations by examining the cross section upon fracture in a field-emission scanning electron microscope (FESEM).

EXPERIMENTAL RESULTS

Critical Current

The critical currents of Strands A and B reacted in 5% hydrogen-95% argon gas on Incoloy 908® barrels, and then transferred to Ti-6Al-4V alloy barrels, are plotted as functions of magnetic field in FIG 1. Also shown are the critical currents of control samples reacted in 100% argon gas. Kramer plots [5] of these data are given in FIG 2. The curves in FIG 1 were obtained from the Kramer plot fits shown in FIG 2. In FIG 3, critical currents of specimens reacted in 5% hydrogen-95% argon gas are compared with those of control samples reacted in 100% argon gas.

As seen in these figures, the measured critical currents of specimens reacted in 5% hydrogen-95% argon gas are smaller than those reacted in pure argon gas. The I_c reduction of Strand A was more pronounced with decreasing field: 12% at 12 T and 14% at 5 T. The I_c reductions of Strand B were 4% at 12 T and 10% at 8 T. The irreversibility field B^* obtained by extrapolations of straight lines to zero critical current on Kramer plots are summarized in TABLE 1 below. The values of B^* obtained from the experimental data over the limited field range showed slight increases with hydrogen treatment.

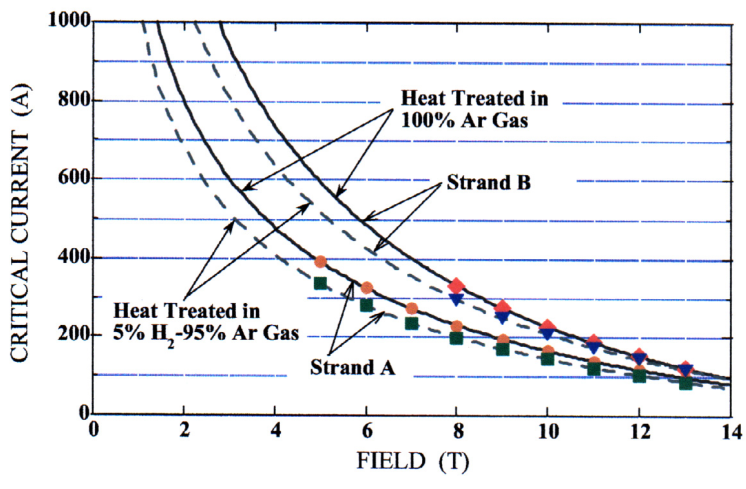

FIGURE 1. Critical currents of Strands A and B reacted on an Incoloy 908® barrel in 5% hydrogen-95% argon gas flow and transferred to a Ti-6Al-4V alloy barrel are plotted with the critical currents of control samples reacted in 100% argon gas flow as a function of magnetic field. The lines were obtained from the Kramer plot fits in FIG 2.

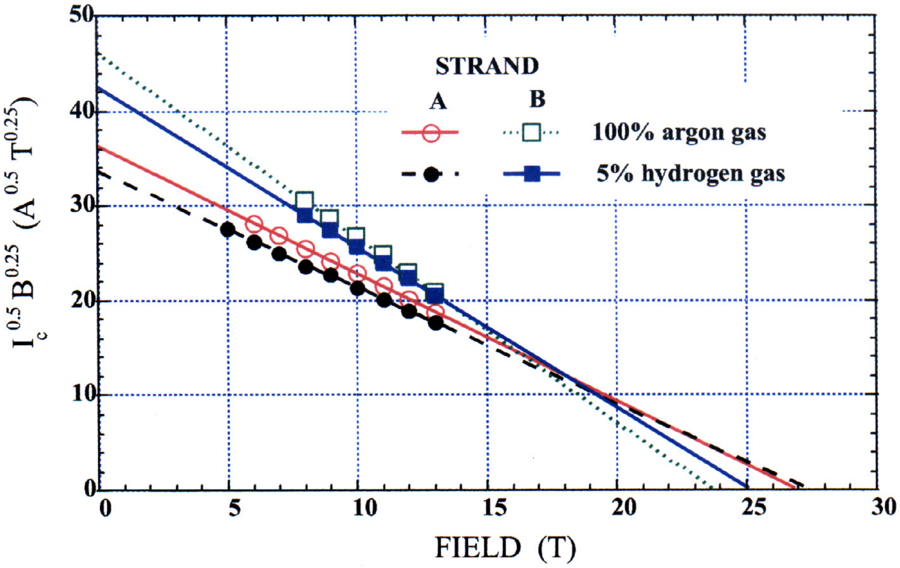

FIGURE 2. Kramer plots of the critical current data shown in FIG 1. The irreversibility fields B* are given by the intercept on the field axis.

The n-index values of the I-V curves for both Strands A and B are plotted as a function of field in FIG 4. Within the scatter, the n-values seem not to be affected by the 5% hydrogen gas heat treatment.

DC Magnetization

The DC magnetization of the samples without Cr plating was evaluated in the VSM. At 12 K, the whole hysteretic part of the magnetization to the irreversibility field B^* can be obtained and the quality of the fit to the Kramer function established. Since the hysteretic magnetic moment, Δm, of the sample is proportional to the product $J_c V d_{\mathrm{eff}} n_{\mathrm{f}}$, where V is the volume of superconductor, d_{eff} the effective filament diameter, and n_{f} the number of filaments. A plot of $\Delta m^{0.5} B^{0.25}$ versus B should be linear. As seen in FIG 5, the linearity is excellent, thus justifying the extrapolation method of determining B^* for these samples.

The values of B^* obtained in this way are collected in TABLE 1. Treatment in 5% hydrogen reduced B^* slightly for both wires at both 4.2 K and 12 K, for example, at 4.2 K from 24.7 to 24.5 T for Strand A and from 20.7 to 20.5 T for Strand B.

TABLE 1. The irreversibility field B^* obtained from Kramer plots of the magnetization measurements and the critical currents.

		MAGNETIZATION		CRITICAL CURRENT
STRAND	ATMOSPHERE	B^* at 4.2 K (T)	B^* at 12 K (T)	B^* at 4.2 K (T)
A	5% hydrogen-95% argon	24.5	9.9	27.5
A	100% argon	24.7	10.1	27.0
B	5% hydrogen-95% argon	20.5	8.8	25.2
B	100% argon	20.7	9.3	23.8

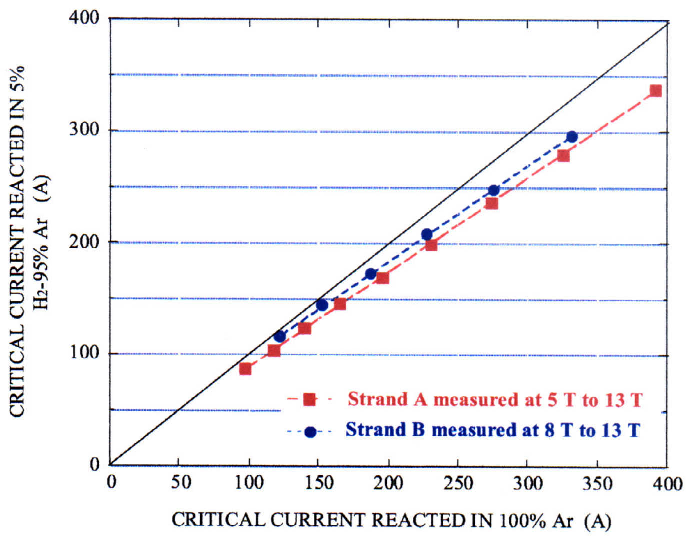

FIGURE 3. Critical currents of Strands A and B reacted in 5% hydrogen-95% argon gas as a function of critical currents of control samples reacted in 100% argon gas. Strand A data were obtained from 5 T to 13 T, and Strand B data from 8 T to 13 T.

Hysteresis Loss

Hysteresis losses of Strands A and B with and without Cr-plating were measured for a full field cycle of +3 T to –3 T to +3 T. In FIG 6, hysteresis losses of specimens reacted in 5% hydrogen-95% argon gas are compared to the control samples reacted in 100% argon gas.. In FIG 6, hysteresis losses of specimens reacted in 5% hydrogen-95% argon gas are compared to the control samples reacted in 100% argon gas. Hysteresis losses of the Cr-plated specimens reacted in hydrogen were reduced to 86% for Strand A and to 92% for Strand B, compared with those reacted in pure argon. The bare wires of Strands A and B showed slightly greater reductions in Hysteresis loss than those of the Cr-plated wires.

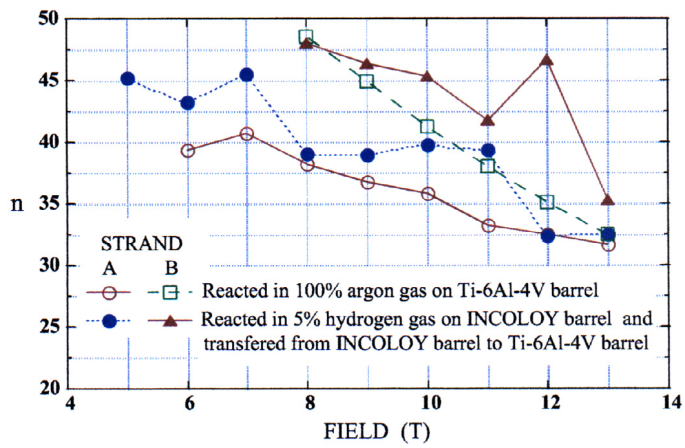

FIGURE 4. The *n*-index values of Strands A and B reacted on an Incoloy 908® barrel in 5% hydrogen-95% argon gas flow and transferred to a Ti-6Al-4V alloy barrel as a function of magnetic field, compared to those of a control sample reacted in 100% argon gas flow.

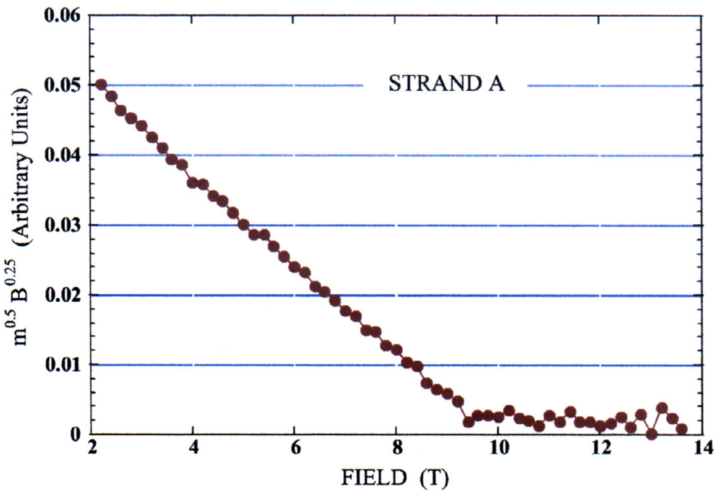

FIGURE 5. Hysteresis losses of Strands A and B reacted in 5% hydrogen-95% argon gas as a function of hysteresis losses of control samples reacted in 100% argon gas.

Residual Resistivity Ratio

The RRR values of Strand B reacted in hydrogen were about 144 for Cr-plated wire and 570 for non-Cr-plated wire. These RRR values were similar to those for wires reacted in 100% argon gas. No effect of hydrogen on the RRR was observed.

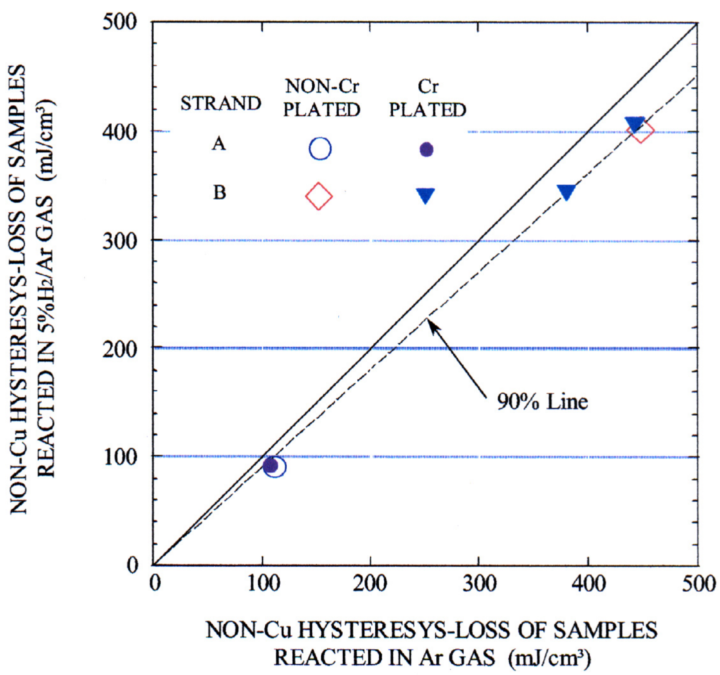

FIGURE 6. Hysteresis losses of Strands A and B reacted in 5% hydrogen-95% argon gas as a function of hysteresis losses of control samples reacted in 100% argon gas.

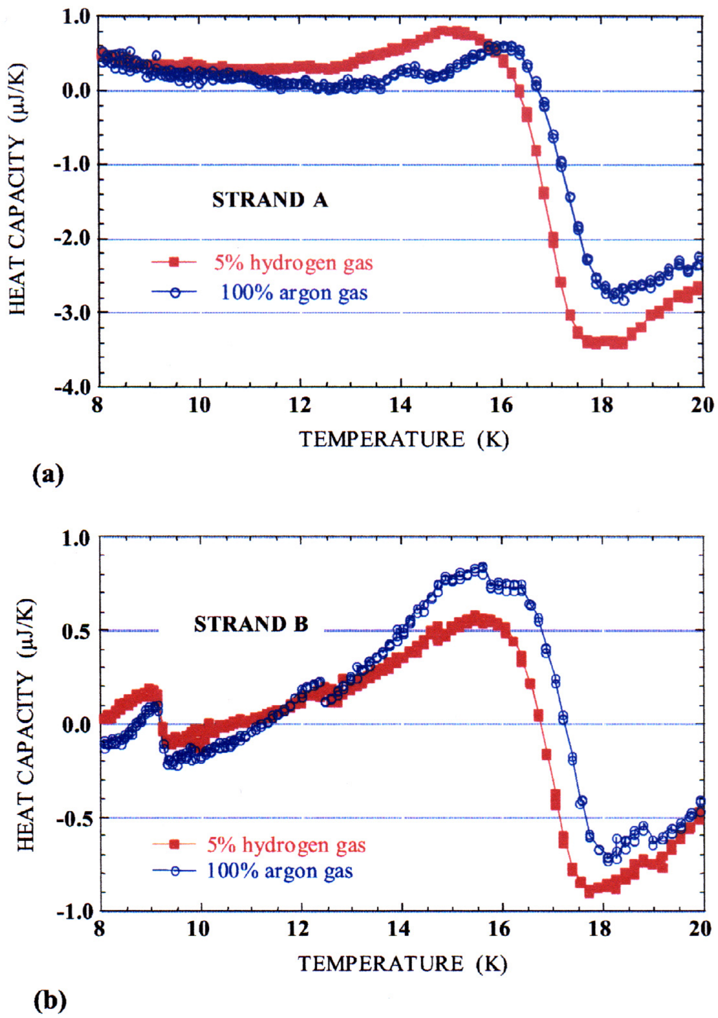

FIGURE 7. Heat capacity as a function of temperatures of (a) Strand A and (b) Strand B.

Specific Heat

The specific-heat measurement of T_c is shown in FIG 7. In both cases it can be seen that the onset and main body of the transition are suppressed by about 0.5 K. Both wires exhibit rather smeared transitions down to about 16 K, indicative of T_c and probably B_{c2} gradients that have their origin in composition gradients across the filaments [6]. The Nb barrier transition at 9.2 K in FIG 7(b) is also quite clear in Strand B.

Microstructural Analysis

The microstructural observations revealed no significant variations in microstructure between the samples reacted in 5% hydrogen gas and the control samples reacted in 100% argon gas.

DISCUSSION AND CONCLUSIONS

It is clear that the effect of hydrogen heat treatment was to decrease the critical-current density and the critical temperature. The critical-current reductions of Strand A were about 12% at 12 T and 14% at 5 T, whereas those of Strand B were 4% at 12 T and 10% at 8 T. The influence of the hydrogen treatment on the irreversibility field B^* was not so clear. In the magnetization measurements for both wires, B^* was reduced at both 4.2 K and 12 K. By contrast, the Kramer extrapolations from the transport measurements indicate a small enhancement of B^* for hydrogen treatment. B^* obtained from the transport measurements were significantly higher than that obtained from the magnetization measurements. Since the electric field of the two measurements differed by only a factor of two (10 and 18 μV/m) it is assumed that the principal factor is the smaller residual strain state of the Nb_3Sn filaments within the wires when tested with applied tension on the Ti-6Al-74V barrel, as compared to the precompressed state of the filaments when tested in the VSM. Detailed analyses of the large differences between the transport and magnetization methods for obtaining B^* would require further investigation.

Hysteresis losses measured for a full field cycle of +3 T to −3 T to +3 T were reduced by 14% for Strand A and by 8% for Strand B by hydrogen heat treatment. The hysteresis loss reduction might result from the critical current reductions in that field range. The heat treatment in hydrogen showed no significant effects on the residual resistivity ratio or microstructure.

ACKNOWLEDGEMENTS

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REFERENCES

1. Jayakumar, R. J., and Wohlwend, J., "ITER CS Coil R&D and Model Coil Effort," 13th Topical Meeting on the Technology of Fusion Energy, 1998.
2. Bruzzone, P., ten Kate, H. H. J., Nishi, M., Shikov, A., Minervini, J., and Takayasu, M., *Adv. Cryo. Eng.* **42**, 1351-1358 (1996).
3. Goodrich, L. F., Medina, L. T., and Stauffer, T. C., *IEEE Trans. Appl. Supercond.* **7**, 1508-1511 (1997).
4. Goldfarb, R. B., and Itoh, K., *J. Appl. Phys.* **75**, 2115-2118 (1994).
5. Kramer, E. J., *J. Appl. Phys.* **44**, 1360-1370 (1973).
6. Hawes, C. D., Lee, P. J., and Larbalestier, D. C., *IEEE Trans. Appl. Supercond.* **10**, 988-991 (2000).