Efficacy of Tantalum Tungsten Alloys for Diffusion Barrier Applications

D B Smathers and P R Aimone
H. C. Starck, Inc. 45 Industrial Place, Newton, MA 02461 USA
E-mail: david.smathers@hcstarck.com, paul.aimone@hcstarck.com

Abstract. Traditionally either Niobium, Tantalum or a combination of both have been used as diffusion barriers in Nb3Sn Multi-filament wire. Vanadium has also been used successfully but the ultimate RRR of the copper is limited unless an external shell of Niobium is included. Niobium is preferred over Tantalum when alternating current losses are not an issue as the Niobium will react to form Nb3Sn. Pure Tantalum tends to deform irregularly requiring extra starting thickness to ensure good barrier qualities. Our evaluations showed Tantalum lightly alloyed with 3 wt% Tungsten is compatible with the wire drawing process while deforming as well as or better than pure Niobium. Ta3wt%W has been processed as a single barrier and as a distributed barrier to fine dimensions. In addition, the higher modulus and strength of the Tantalum Tungsten alloy improves the overall tensile properties of the wire.

1. Introduction

The progression of technology from discovery to multi-filamentary wire was very rapid for Nb3Sn. The history of Nb3Sn and the need for finely divided filaments is very nicely summarized in two recent theses. The brittle nature of Nb3Sn required the clever invention of creating the multi-filamentary structure first and then converting ductile niobium into Nb3Sn by solid state diffusion of tin through a copper matrix. The quality of the Nb3Sn filaments can be very good, especially when very high fractions of niobium can be incorporated and an excess of tin provided. A need arose at the start to prevent the excess tin from contaminating the parallel, stabilizing copper conductor. A barrier between the highly active tin and the high purity copper was needed to prevent diffusion of tin through the barrier layer during the reaction heat treatment. Tantalum was an early choice and theoretically more ideally suited for the purpose than niobium. Tantalum has a lower critical temperature than niobium and any reaction between tantalum and tin to form Ta3Sn also results in a low critical temperature. Tin diffusion through tantalum is slower than through niobium due to the differences in melting temperature. However, tantalum did not co-process as well as pure niobium. Some solutions were found to improve the formability of pure tantalum and it is primarily incorporated when low a.c. losses are required in the reacted conductor.

One of the issues often seen with pure tantalum is wall thickness instability of the barrier layer. The consequence of this instability is a tendency to use thicker tantalum in the barrier layer to be sure a minimum thickness is available in all locations. The excess tantalum is neither stabilizer nor superconductor and adds undesired cost to the wire. Complicated or expensive alternatives include pure vanadium, a combination of vanadium and niobium, a combination of tantalum and niobium or a Ta40Nb alloy.
In this work, we study the potential of using tantalum lightly alloyed with 3 weight percent tungsten (Ta3W) as a diffusion barrier material in place of pure tantalum. We initially studied this alloy as a wire reinforcement material and found the stability of the copper-tantalum interface is superior for the Ta3W alloy. The improved interfacial stability reduces the need for excess thickness resulting in an improved cost model. The primary benefit was higher wire mechanical properties with the Ta3W alloy as either a parallel filament or a diffusion barrier. Tubular Ta3W was successfully co-processed with a multi-filamentary copper niobium and copper niobium tin composite and tested for the efficacy of the diffusion barrier properties. Since Ta3W is a commercial alloy in regular production the comparative cost to pure tantalum is quite good. H. C. Starck produces and sells this alloy under the trade mark NRC76™.

2. Wire Construction

The wire process used to make test specimens was previously reported. The process was improved by increasing the copper to niobium local ratio and improving the bonding process using low temperature heat treatments and limiting consolidation to drawing. The earlier trials were consolidated by swaging the assembly full length.

To test the process capability of a tantalum tungsten diffusion barrier, a seam welded Ta3W tube (12.7mm diameter by 0.38mm wall) was added to a second stage assembly between a 19 x 19 (2.29mm f-f) stack and a “stabilizer” copper tube (16.5mm x 1.5mm wall). This assembly was cold drawn to 0.72mm as a mono-barrier assembly, figure 1 (a). Some of this construction was converted to 3.05mm hexagonal element from 3.66mm diameter wire and re-stacked as an 18 element in a similar pure copper tube (18.3mm outer diameter by 1.5mm wall). The two stage assembly was cold drawn to 0.72mm as a distributed barrier composite. These wires only evaluated the ability of the Ta3W alloy to co-process with the copper-niobium as no tin elements were incorporated. An unexpected result was the survivability of the seam weld microstructure through ~500:1 area reduction. Figure 1 shows the wire cross section of the mono barrier assembly and distributed barrier assemblies at 0.72mm diameter. While the mono-barrier wire shows a continuous barrier, figure 1a, the distributed barrier shows some failure, usually near the weld area. There was no filler between the 19 element hexagonal geometry and the round tube. The Ta3W conformed to the stack but this extra deformation may have introduced some unintentional strain into the elements leading to barrier failure, figure 1 (b).

![Figure 1](image-url)

**Figure 1.** (a) Mono barrier wire with copper-niobium elements and (b) distributed barrier version wires at 0.72mm diameter. Optical micrographs.
The success of the early experiment lead to the desire to test the Ta3W alloy as a real diffusion barrier. Tin-titanium elements were provided by Luvata. The only wire assembly method available for this experiment was stacking hexagonal elements in round tubes. Providing a large tin core to a filament array is often done by gun drilling an extruded assembly. For this experiment, all the hexagonal elements needed to be the same diameter. A 37 element stack was chosen with the 7 element core being copper clad tin-titanium rods. This non-optimum choice would lead to issues in the wire drawing. To make the 37 element stack more circular, the 6 peak elements were drawn to a smaller diameter. 31 elements (7 tin-titanium and 24 copper-niobium) were drawn to 1.57 mm face to face hexagonal and 6 elements (copper niobium) to 1.29 mm face to face. In this assembly, an overlapped rather than welded tube, 0.38mm thick by 12.7mm diameter, was used. Figure 2 shows the mono-barrier version at 0.72mm diameter. The distributed barrier version was not drawn below 2.6mm diameter due to excessive breakage. The breakage was a result of stacking faults in the assembly rather than the diffusion barrier material. During the assembly process, some of the elements shifted from their ideal position leading to the 7 tin cores being inadequately contained, figure 2.

![Figure 2](image-url)

**Figure 2.** Mono barrier wire with copper-niobium and tin-titanium elements at 0.72mm diameter. (a) As drawn, optical image. (b) 210°C/72hr, SEM image [inverted contrast]

The 0.72mm mono-barrier was drawn with sufficient length to run a reaction heat treatment to test the barrier quality. At 0.72mm, the Ta3W barrier thickness is ~0.02 mm and the niobium filaments are ~0.015 mm. The niobium filament size is much larger than would be appropriate for a true Nb-Sn conductor. The goal of the experiment is to test fabrication and efficacy, not make a competitive superconductor wire.

3. Results

3.1 Wire Processing

The general fabrication of the wires went very well. The experimental design choices that led to issues at small diameters can be easily overcome by more experienced practitioners. The key parameter of interest was whether the Ta3W co-processes with the pure copper and niobium elements. The wall thickness and area uniformity of the Ta3W material stayed consistent after the wire was fully dense. The Cu-Ta3W interface is much more uniform than a conventional Cu-Ta interface.

Even though the Ta3W hardness is high compared to the niobium and especially copper, it still processes consistently. At low strains, typical of wire drawing passes, the small difference in flow stress between tantalum and Ta3W suggests they process equivalently. The welded tube survived a
500:1 area reduction. The overlapped tube design in the wire that incorporated the tin elements also processed well through 500:1 area reduction. The overlap introduced some sharp edges and the wall thickness is doubled leading to local stiffening that could impact the internal stresses during wire fabrication. A slightly worked weld could make the welded tube design much more practical.

3.2 Mechanical Properties

The increased mechanical strength of Nb-Cu wires with the substitution of Ta3W has been previously shown12. In the previous work the strengths were shown with a reported 700°C heat treatment. A correction was submitted to properly report the heat treatment as 8 hours at 250°C. When the wires were heat treated for 3 hours at 700°C, the wire without tantalum reinforcement softens much more substantially while the wire with Ta3W barriers maintains more of its strength13, figure 3. This is true when the reinforcement Ta3W element is a large filament, a tube or diffusion barrier, whether single or distributed.

![Figure 3](image)

**Figure 3.** Mechanical properties for Cu-Nb multi-filamentary wires without (a) and with (b) Ta3W elements. A wire with a Ta3W element maintains more strength at high reaction temperature as compared to a wire without a Ta3W element. Heat treated 8 hours at 250°C or 3 hours at 700°C.

3.3 Diffusion Heat Treatment and RRR

Heat treatment and RRR measurements were performed at the Applied Superconductivity Center at Florida State University. Two heat treatments were run on the wire prior to testing the residual resistivity ratio (RRR) to determine the value before and after tin had the potential to penetrate the barrier. The first heat treatment was at 210°C for 72 hours and was meant to simply anneal the copper without stressing the diffusion barrier since only short range solid state diffusion was possible. The second heat treatment was representative of a real superconductor wire, 210°C for 72 hours followed by 400°C for 48 hours and then 640°C for 48 hours. The RRR was measured using a 4-point probe with a current of 0.5 amp. The reacted sample was observed to begin the superconducting transition at about 17.2 K. The resistance values were compared at 300K and 19K. After the 210°C/72 hour treatment, the wire RRR was 113 +/- 3. Following the reaction heat treatment, the RRR increased to 247 +/- 7. The wire geometry may be playing a role. The un-reacted wire has more copper to participate in the room temperature conductivity. When the mean free path increases as the temperature is reduced the copper between the niobium filaments may contribute less to the conductivity. The fine filament structure effectively alters the amount of copper in the measurement between 300K and 19K. At 19 K, the wire resistance is about the same but at 300K, the conductivity of the un-reacted wire is lower than the reacted wire. As can be seen in figure 2, the grain size of the
stabilizing copper is much smaller than after the full reaction heat treatment, figure 4. Nevertheless, the Ta3W barrier has withstood the tin activity and preserved the copper purity.

Figure 4. Scanning electron microscope images of reacted 0.72mm diameter wire. Full cross section (a) and higher magnification image (b) shows the bronze formation near the barrier and reaction of the smaller niobium filaments. The outer pure copper shell has a RRR of 247 +/-7 and large grains. Voids appear white due to inverting the SEM image contrast to compare more easily with the optical images. The large niobium filaments show little reaction near the barrier but the small niobium filaments in the element keys are almost completely reacted.

4. Discussion

Ta3W has great potential to replace pure Ta as a single layer diffusion barrier option due to its better interfacial stability during wire drawing and the added strength and temperature stability provided in the reacted wire product. A model wire incorporating a single Ta3W diffusion barrier has been processed with reactive tin cores through more than 500:1 area reduction and survived a standard reaction heat treatment while preserving the purity of the outer copper stabilizer. Experienced practitioners can incorporate the benefits of Ta3W diffusion barriers into future low a.c. loss wire designs. The high survivability of a weld microstructure during co-processing could also make a continuous tube forming concept more productive.

Acknowledgments

Measurements at Florida State University were supported by the Department of Energy under Award Number DE-SC0012083 and were performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida. Many thanks to William Starch and Brandon Chew for assistance in wire drawing, Christopher Segal for RRR measurements, Shreyas Balachandran and Peter Lee for analysis and discussion. Optical microscopy was performed under contract with Paul Danielson at eImaging in Bend Oregon. Special thanks to Tae Pyon at Luvata Special Products for the supply of tin-titanium rod.

References

[1] Sanabria C, 2017 A new understanding of the heat treatment of Nb-Sn superconducting wires, PhD thesis, University of Florida-Tallahassee
[2] Godeke A, 2005 Performance boundaries in Nb3Sn superconductors, PhD thesis, University of Twente, Enschede, The Netherlands
[3] McDougall I, 1975 Method of fabricating a composite intermetallic-type superconductor, US Patent 3,876,473
[4] Young M and Larbalestier D, 1981 Wrapped tantalum diffusion barrier, US Patent 4,285,740
[5] Nijhuis A, Knoopers H and ten Kate H, 1994 The influence of the diffusion barrier on the AC loss of Nb3Sn superconductors, Cryogenics 34 (1), 547-550
[6] Hartwig K, Balachandran S, Mezynski R, Seymore N, Robinson J and Barber R, 2014 Fabrication of fine-grain tantalum diffusion barrier tube for Nb3Sn conductors, Adv. in Cryogenic Eng., vol 60 1574: 204-210
[7] Balachandran S, Hartwig K, Baars D, Mathaudhu S, Bieler T, Pyon T and Barber R, 2009 Fabrication of tantalum sheet for superconductor diffusion barriers, IEEE Trans on Appl Superconductivity 19 (3) 2606-2609
[8] Smathers D, O’Larey P, Siddall M and Peterson R, Characterization of vanadium diffusion barriers in Nb-Sn composite wires, 1987 IEEE Trans. Mag, Vol MAG-23, no. 2, 1347-1350
[9] Smathers D, O’Larey P, Siddall M and McDonald W, 1988 Status of the superconductor development program at Teledyne Wah Chang Albany, Adv. in Cryogenic Eng., vol 34 515-522
[10] Hartwig K, Balachandran S, Barber R, Pyon T and Griffin R, 2011 Design aspects of dual Nb-Ta sheet diffusion barriers for Nb3Sn conductors, IEEE Trans. Appl. Superconductivity, 21(3): 2563-2566 Part 3
[11] McKinnell J, O’Larey P, Jablonski P and Siddall M, 1997 Tantalum-niobium diffusion barriers for superconducting Nb3Sn wires in fusion applications, Adv. in Cryogenic Mails, Vol 42, 1415-1422
[12] Smathers D, Aimone P, 2017 Comparison of Ta3wt%W and Pure Ta as a Wire Reinforcement Element in a Multifilament Composite, IEEE Trans. on Appl. Superconductivity Vol 27 (4)
[13] Smathers D, Aimone P, 2017 Replacement of Ta Elements with Ta-W Elements in Nb3Sn Superconductors, to be published in: Proc. 19th Plansee Seminar (eds. L.S. Sigl et al., Reutte 2017).
[14] Weiss K, Nyilas A, Thoener M and Seeber B, Proof Strength behaviour of Nb3Sn bronze route wires between 300 and 4K, Adv. in Cryogenic Eng. Vol 43: Transactions of the international Cryogenic Materials Conference Volume AIP Conference Proceedings 986: 293 2008
[15] Pyon T, Luvata Special Products, Waterbury, CT, private communication 2017.
[16] Fu X, Gregory E, McIntyre P, Smith D and Tomsic M, 2004, Continuous tube forming of the Ta diffusion barrier and Cu stabilizer on Internal-Nb3Sn subelement, AIP Conf. Proc. 711, 382