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Neutron diffraction studies of the Zr/Nb effects on the Nb₃Sn phase formation of monofilament wires

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Abstract. The layer growth of the A15 (Nb₃Sn) superconducting phase produced by the internal tin method on model monofilament wires was studied by neutron diffraction and electron microscopy techniques. Different ratios of the inner part of the wire (Sn/Cu) and the effect of the addition of 1% of zirconium to niobium were studied. The high temperature heat treatment plays a key role on the A15 formation and on the cost of the final wires produced. Different temperatures in the range 650-725°C and different annealing times in the range 8-200 hrs have led to the preparation of 72 different samples. The neutron diffraction study has evidenced the different phases formed during the heating treatment and the electron microscopy study has evidenced a power law for the growth rate of the A15 phase. In both studies the addition of zirconium in niobium is very effective on the growth rate of the A15 phase.

Introduction

The heat treatment (HT) of internal tin process composites to form Nb₃Sn requires the mixing of Sn from the filament bundle core with the interfilamentary Cu in order for each Nb filament to be adequately surrounded by Sn prior to Nb₃Sn formation. Due to extremely slow kinetics, the best mixing heat treatment is complex and varies strongly with composite geometry, composition and/or manufacturer [1]. Following the US requirements to develop Nb₃Sn for the high-energy program [2], the heat treatment times must be shorter than 200 hrs. In order to achieve the best A15 Nb₃Sn with high superconducting properties it is important to improve the kinetics of the diffusion mechanism but without lowering the critical parameters (T_c , B_{c2} , H_{c2}). Several dopants are added to Sn, Cu or Nb to enhance the properties. Very early, Suenaga and al. [3] have studied the CuSn bronzes with Nb alloys containing Ti, V, Zr, Mo or Ta and shown that Ti and Ta were increasing T_c and H_{c2} . These dopants (Ti, Ta) of Nb are always used for high field applications [4,5]. Copper in the internal tin process has been doped by Ge and Ti [6,7] and has a strong effect on J_c but slows down the diffusion rate for Nb₃Sn formation. The Northwest Institute for Nonferrous Metal Research (NIN) is working on different dopant using the internal tin process. Titanium has been alloyed with Sn and shows an important increase of the Nb₃Sn formation [8]. In this study the effect of Zr as a dopant of Nb and Ti as a dopant of Sn are presented. Powder neutron diffraction study is a powerful technique that allows recording diffraction patterns of all the volume of the sample, combined with more conventional techniques such as electron microscopy.

Experimental

Monofilament wires were manufactured using the internal tin process and were composed of one sub-element with a central tin reservoir containing 2at% of titanium (Fig. 1). No outer diffusion barrier was used. Three samples with different tin to copper ratios (15, 20 and 25% in weight) (named SF1, SF2, SF4 respectively) were used to study the influence of the Sn/Cu content and one

sample prepared with Sn/Cu=20% with 1% Zirconium allied niobium (named SF3), in order to be compared with the pure niobium wire SF2. The wires have been cold drawn to a final diameter of 0.895 millimeter.

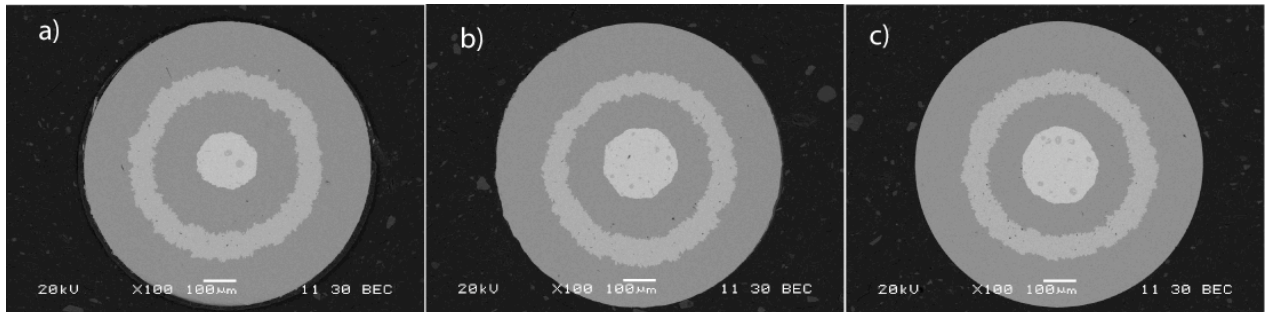


Fig 1. SEM photographs of the a)SF1, b)SF2 and c)SF4 wires with Sn/Cu ratios of 15, 20 and 25 % respectively.

We have prepared 72 samples composed of 6 wires, cut into 60 mm lengths pieces, whose ends have been crimped over 3 mm, and sealed in quartz tubes under argon. Different heating treatments were performed with temperature dwells at 210°C (25 h), 350°C (50 h) and different times of exposure (8 hrs, 32 hrs, 100 hrs and 200 hrs) at different temperatures (650, 675, 700 and 725°C). For the neutron experiment, the bundle of wires in the quartz tube was exposed vertically to the neutron beam in a special sample holder. Neutron diffraction patterns have been recorded at room temperature on the D1B diffractometer of the ILL-Grenoble, at a wavelength of 2.524 Å. Refinements have been done by the Rietveld technique using the Fullprof program [12]. For the scanning electron microscopy studies, samples were open in air and embedded in resin vertically before polishing. Characterization of the microstructure and of the local chemical composition were carried out by X-ray fluorescence analysis using a Kevex EDX probe attached to a JEOL A840 scanning electron microscope.

Results

The diffractograms recorded by neutron diffraction reflect the whole volume sample contained in the quartz tube. An empty quartz tube was used as a reference to be subtracted to the samples. We have refined the structure of the phases observed with the following starting parameters. The Cu and α -Cu phases, space group (SG) Fm3m, $a=3.610$ Å and $a=3.618$ Å respectively, preferred orientation [100]. The Nb and Ta phases, SG=Im3m, $a=3.300$ Å, preferred orientation [100]. The γ -CuSn phase as Cu₃Sn, SG=Fm3m, $a=3.669$ Å. The δ -CuSn phase as Cu₄₁Sn₁₁, SG=F-43m, $a=18.148$ Å. The Nb₃Sn phase, SG=Pm3n, $a=5.293$ Å, preferred orientation [100]. For each phase, only the scale factor (SF), the cell parameter a (all phases being cubic) and the preferred orientation (PO) have been fitted with the instrument parameters known from calibration experiments. Depending on the thermal treatment applied to the sample, 3, 4 or 5 phases have been used to refine the whole pattern. The figure 2a is an example of the observed, calculated and indexed plots obtained by neutron diffraction on the SF3 (Sn/Cu=20%+1%Zr) sample heat treated at 725°C for 200 hrs. In this example, the δ -CuSn phase has been fully decomposed and the Nb₃Sn has almost replaced all the Nb phase. The inset of figure 2b is the same sample heat treated at 700°C for 32 hrs, the δ -CuSn phase is clearly present between the α -Cu and γ -CuSn phases, the niobium peak is intense and the Nb₃Sn is very low. The inset of figure 2c is the same sample heat treated at 700°C for 200 hrs, the δ -CuSn phase has disappeared.

The phase analysis of all the samples has been made by this method and the percentage of the Nb₃Sn phase calculated is plotted in figure 3a as a function of temperature and time for the 4 samples. The best result is for the SF3 (Sn/Cu=20%,1%Zr) sample for which the Nb₃Sn phase formation is observed at 675°C after 100 hrs. At 700°C, after 8 hours some Nb₃Sn is formed. The

higher percentage is observed for 200 hrs at 725°C. The results for the SF2(Sn/Cu=20%) and SF4 (Sn/Cu=25%) samples are very comparable at the lower temperatures, only at 725°C for 100 and 200 hrs, the Nb₃Sn percentage is higher.

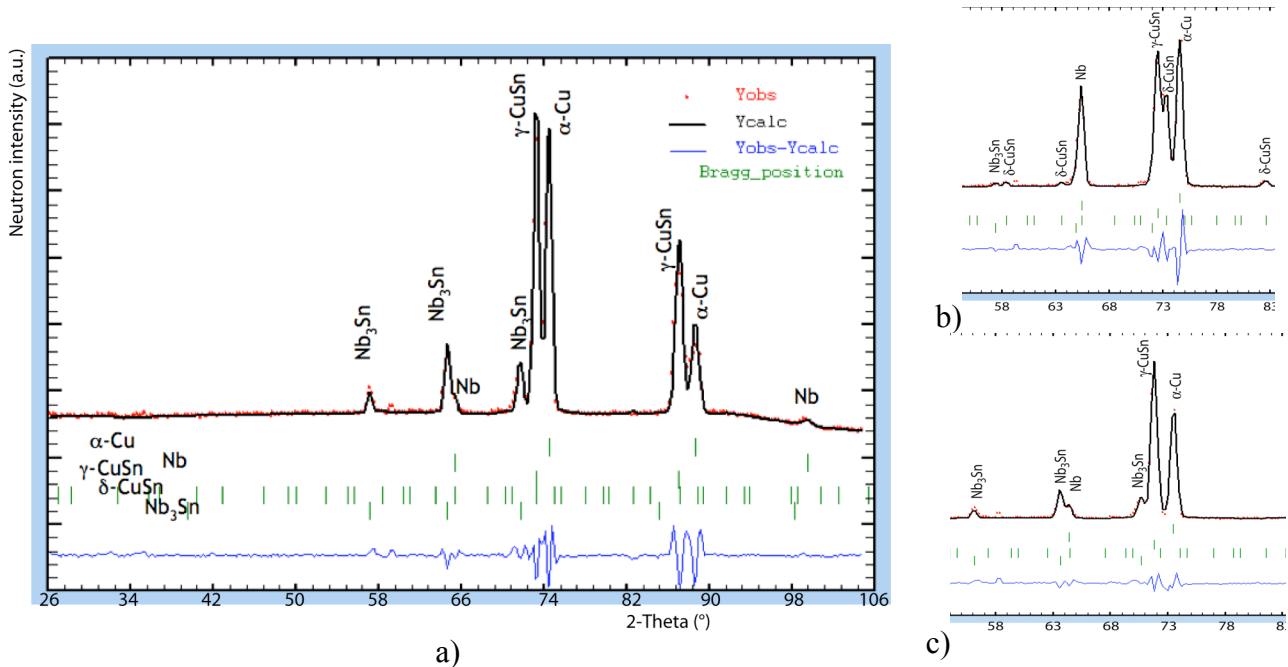


Fig 2: Neutron diffraction patterns recorded after the heat treatment of: a) SF3 sample 725°C, 200 hrs b) SF3 sample 700°C, 32 hrs, c) SF3 sample 700°C, 200 hrs. (Dots = experimental points, line above = calculated, line below = difference, vertical tics = Bragg positions of the different phases)

We have plotted the Nb₃Sn percentages (log scale) for the SF3 sample as a function of the annealing times (log scale) at different temperatures. For the lower temperatures, only the longer times show the presence of Nb₃Sn and the lines drawn reflect only a tendency, but for the higher temperatures, the points can be aligned in this log-log plot indicating a power law formation mechanism.

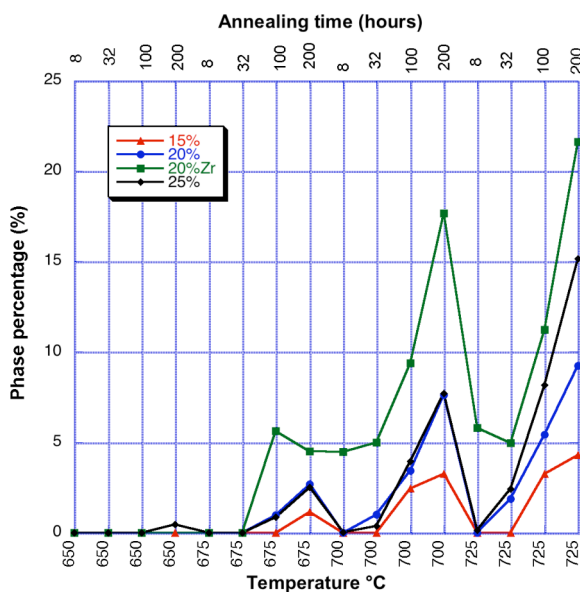


Fig. 3a: Nb₃Sn percentages formed during the different heating treatments calculated from neutron diffraction patterns refinements.

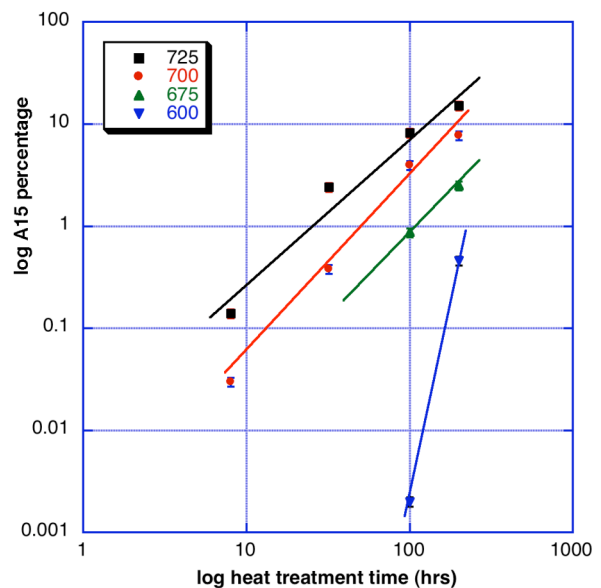


Fig. 3b: Nb₃Sn (A15) phase percentages for the different annealing times and temperatures for the SF3 sample. The lines are just a guide for the eyes.

The heat-treated wire samples have been analyzed by SEM in order to measure the thickness of the A15 layer. As seen on figures 4a and 4b, it is possible to follow the diffusion mechanism by a change in grey levels. The outer layer shown in the photographs is the niobium layer; the white ring appearing is the Nb₃Sn layer. On figure 4a, the effect of time at a constant temperature is shown. After only 8 hrs at 700°C on the SF3, we cannot see in the center of the sample the ring of tin as in fig.1, an alloy with copper is formed. With further time increase, the grey phase (δ -CuSn) is replaced by a darker phase (γ -CuSn) and the white layer of Nb₃Sn appears in the niobium ring. For the 200 hrs sample, the entire layer is almost white, with just a small layer of niobium. The tin diffusion in niobium is very homogeneous; the ring follows exactly the shape of the inner part of niobium ring.

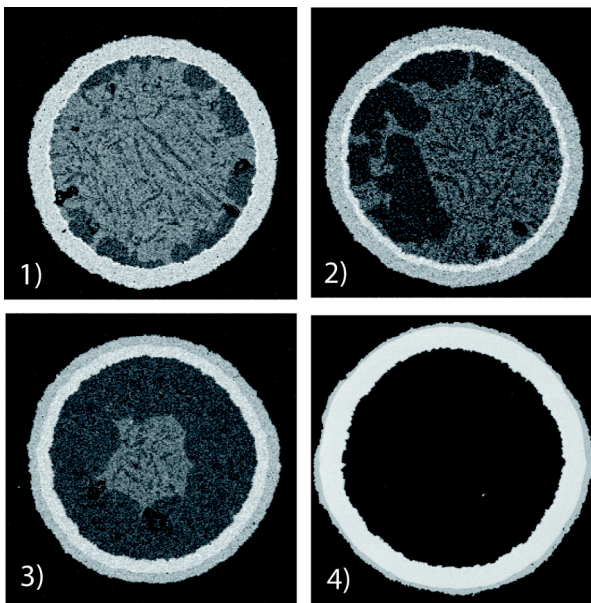


Fig.4a: SEM photographs of SF3 (20%Sn and 1%Zr) heat-treated at 700°C for different times. 1) 8 hrs, 2) 32 hrs, 3) 100 hrs, 4) 200 hrs.

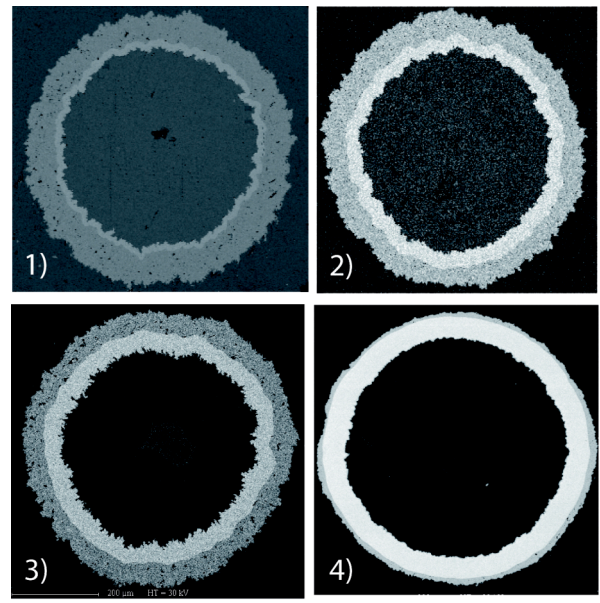


Fig 4b: SEM photographs of the four wires heat-treated at 700°C/200hr. 1) SF1, 2) SF2, 3) SF4, 4) SF3.

In figure 4b, the same heat treatment applied to the 4 samples shows the efficiency of the zirconium addition, the samples 2 and 4 have the same Sn/Cu ratio, but the sample 4 contains 1% of zirconium. The Nb₃Sn formation is almost complete in sample 4, in comparison to sample 2, where only 1/3 of the layer is formed.

All the heat-treated monofilament wire samples were measured for the A15 (Nb₃Sn) layer thickness on the SEM photographs in order to estimate the A15 phase formation growth rate. It is known that the logarithm of the formed A15 layer thickness (y) at an enduring temperature can present a linear relationship with the logarithmic of the heat treatment time ($y=k*t^n$) [9,11], from which the reaction rate coefficient and even the reaction activation energy could be calculated in a known diffusion model. In figures 5a and 5b for the two samples with the same Sn/Cu content we have reported in a log-log representation this variation. For all the temperature for which it is possible to measure the layer thickness, the points seem to be aligned on lines.

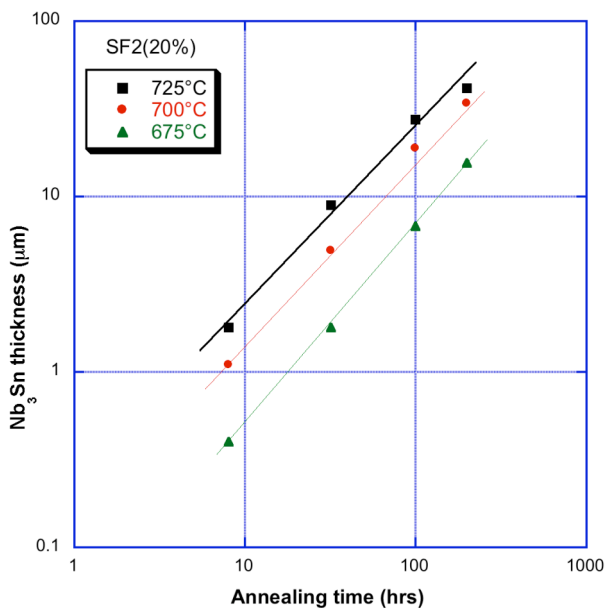


Fig5a: A15 layer thickness as function of heat treatment time for SF2 wire.

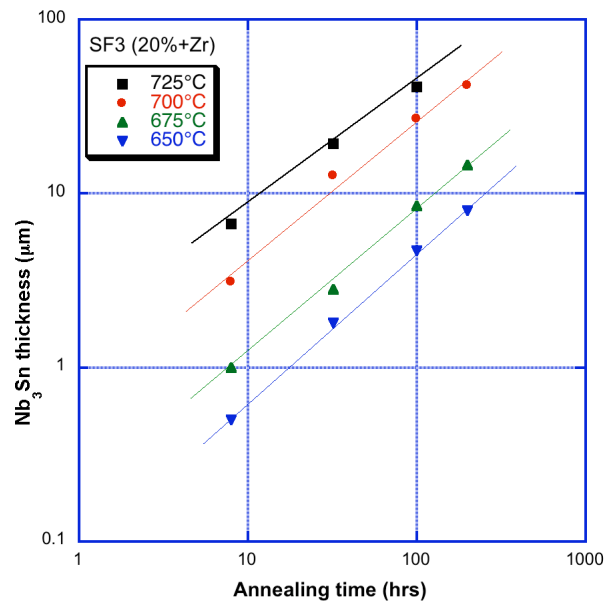


Fig5b: A15 layer thickness as function of heat treatment time for SF3 wire.

Discussion and conclusion

From in-situ neutron diffraction studies [8] we have shown that the decomposition of the δ -CuSn phase leads to the formation of the Nb_3Sn phase and that the kinetics of the reaction presents a power law of formation. In the present study we have determined, by the weighting method of profile refinement [12], the phase percentage of Nb_3Sn at different times and temperatures. This phase percentage (Y) is proportional to the volume of phase and is related to the rate of formation of the phase, however it is not possible to extract some quantitative value about the rate of formation as the volume can not be measured with accuracy due to the small number of diffraction peaks for each phase.

From the SEM experiments it can be seen that the layer growth rate is strongly dependant of the temperature and of the addition element in niobium. All the niobium is transformed at 725°C in 100 hrs in the SF3 sample (with 1%Zr) and in 200 hrs in the SF2 sample. We have plotted the layer thickness of the white part of the sample (considered as the formation of Nb_3Sn) as measured on the SEM images as a function of the annealing time for the samples SF2 (20%) and SF3 (20%+Zr) in fig. 6a and 6b and fitted to a power law with Kaleidagraph. In both cases it is clear that this diffusion power law ($y=(k*t)^n$) applies to these compounds, k and n being the refined values reported in fig. 6. The n exponent decreases with temperature to the contrary of the observations of [10], this can be due to the special round shape of the interface of growth that increases the number of diffusion sites available for tin [13].

On the role of Ti in Sn or Zr in Nb we can observe than the Sn diffusion is strongly accelerated by the presence of a small percentage of zirconium or titanium; Titanium and particularly Zirconium seem to be able to easily reduce the Nb oxidized surface which could act as a diffusion barrier for Sn.

| $y = (k \cdot t)^n$ | | $y = (k \cdot t)^n$ | | $y = (k \cdot t)^n$ | |
|---------------------|------------|---------------------|----------|---------------------|-----------|
| | Value | | Value | | Value |
| n | 0.77519 | n | 0.95253 | n | 1.1888 |
| k | 0.00017543 | k | 5.681e-5 | k | 1.3996e-5 |
| Chisq | 12.882 | Chisq | 2.9733 | Chisq | 0.0064891 |
| R | 0.99336 | R | 0.99777 | R | 0.99998 |

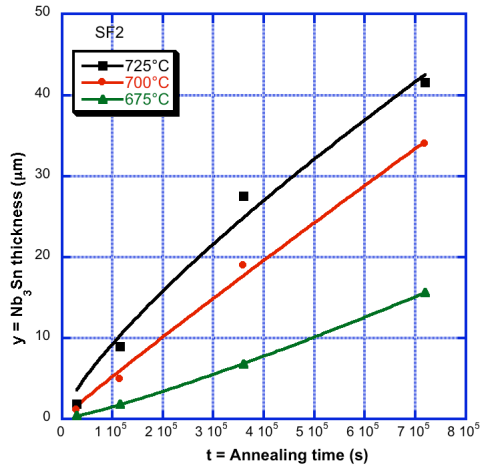


Fig. 6a: Nb_3Sn layer thickness as a function of annealing time for the SF2 sample.

| $y = (k \cdot t)^n$ | | $y = (k \cdot t)^n$ | | $y = (k \cdot t)^n$ | | $y = (k \cdot t)^n$ | |
|---------------------|------------|---------------------|------------|---------------------|-----------|---------------------|-----------|
| | Value | | Value | | Value | | Value |
| n | 0.68687 | n | 0.68624 | n | 0.84494 | n | 0.80095 |
| k | 0.00062622 | k | 0.00032485 | k | 3.3453e-5 | k | 1.8617e-5 |
| Chisq | 0.62114 | Chisq | 3.1324 | Chisq | 0.2164 | Chisq | 0.02759 |
| R | 0.99949 | R | 0.99818 | R | 0.99904 | R | 0.99958 |

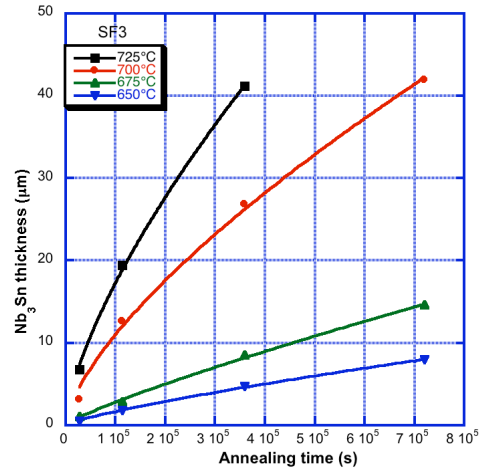


Fig. 6b: Nb_3Sn layer thickness as a function of annealing time for the SF3 sample.

Summary

The growth of the Nb_3Sn phase was studied on a monofilament with different Sn/Cu ratios and for a composition with an additive element in niobium at different temperatures in the range 650 – 725°C and for times ranging from 8 to 200 hrs. Two complementary techniques were used, neutron diffraction and SEM observations. The neutron diffraction gave access to the various phases formed in all the volume of the sample and characterized by special diffraction lines. This technique has enabled to extract the percentage of each phase observed in the 72 samples analyzed. An important result is the link between the decomposition of the $\delta\text{-CuSn}$ phase (with a theoretical decomposition temperature of 590°C) and the formation of the Nb_3Sn phase. The very effective role of the Zr addition element on the speed rate of formation of the Nb_3Sn phase has been evidenced. There is still to demonstrate the effects on the superconducting properties of ITER wires. The SEM technique by measuring the effective Nb_3Sn layer thickness has allowed extracting a power diffusion law for a round interface with decreasing n exponent with increasing temperature. This law has also to be demonstrated on very small interfaces as shown on multifilarities where the interface curvature is less pronounced. The role of oxygen as barrier diffusion in niobium should certainly be reduced by the use of other metals acting as oxygen getters in the niobium. These studies should lead to improvements in the design and composition of wires to reduce the time of the thermal treatment of ITER wires.

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