Kinetics of phase growth in the Cu-Sn system and application to composite Nb_3Sn strands

S. Mattafirri, E. Barzi, F. Fineschi, and J.M. Rey

Abstract-- **Nb_3Sn is the superconductor most used in the R&D of high field accelerator magnets by either the wind&react or the react&wind technique. In order to program the low temperature steps of the heat treatment, the growth kinetics of Cu-Sn intermetallics was investigated as a function of duration and temperature. The diffusion constants of η, ε and δ phases between 150 and 550°C were evaluated using Cu-Sn model samples. Statistical and systematic errors were thoroughly evaluated for an accurate data analysis. Next the behavior of Internal Tin and Modified Jelly Roll Nb_3Sn composites was compared with the model predictions.**

Index Terms— **Cu-Sn intermetallic compounds, diffusion constants, growth kinetics, IT and MJR strands.**

I. Introduction

The reaction cycle required to produce the superconducting Nb_3Sn intermetallic compound by a diffusion process of the Sn through the Cu matrix is a critical step in the manufacturing process of a magnet. The superconducting and mechanical properties of the superconductor are obtained during this operation. For instance, the presence of liquid phases may cause the motion of the Nb filaments allowing contact with adjacent filaments, and the presence of voids may hinder the diffusion between Cu and Sn. In addition, during the low temperature heat treatment, wire bursts due to the liquid phases overpressure can damage the wires.

In order to program the low temperature steps of the heat treatment (HT) for any strand design, the growth kinetics of ε, η and δ phase was studied as a function of HT duration and temperature. The diffusion constants of the Cu-Sn phases were evaluated as fitting parameters by minimizing the χ^2 function of the layer thickness measurements versus HT time and temperature, using the parabolic growth law model. In order to provide "infinite" sources of Cu and Sn, Cu-Sn sample models were used. The models were realized by casting liquid Sn into Cu containers, and heat treating them in pyrex tubes with nitrogen coverage. The mean thickness of the intermetallic layer was obtained by measurements of its cross sectional area in several regions along the interface using a high resolution optical microscope. In cases of ambiguity, phase identification was performed with SEM/EDS analysis. An accurate evaluation of the systematic and statistical errors was performed on each measured parameter and the errors were propagated to the diffusion constants. The value of the reduced χ^2 for each data fit is a measure of how well errors were evaluated and of the capability of the parabolic growth law to describe the observed data distribution.

To check the applicability range of the model onto strands, the growth of the Cu-Sn intermetallic phases was measured for Internal Tin (IT, by ex-Intermagnetics General Corporation, IGC) and Modified Jelly Roll (MJR, by Oxford Superconducting Technology, OST) strands for all the durations and temperatures applied to the model samples. Results of this comparison are shown and commented.

II. Diffusion Model

The intermetallic growth model by diffusion mechanism used to evaluate the diffusion constants of the Cu-Sn phases is the so-called parabolic growth law:

$$y^2 = k(T)t\,, \tag{1}$$

where y is the intermetallic layer thickness, t is the duration and T is the temperature of the HT, and k the rate of growth of the intermetallic layer. This relation derives from Fick`s first law under the hypothesis of a constant concentration of the diffusing components at the interlayer boundaries and of a constant concentration gradient along the interlayer. The two conditions are satisfied because of the narrow composition range (~1%) of the η, ε and δ phase, [1].

An exponential dependence of the rate of growth with the HT temperature [2], is adopted:

$$k = k_0 \exp(-E/kT)\,, \tag{2}$$

where k_0 is the diffusion frequency, T is the temperature, β is the Boltzmann constant and E is the activation energy.

Substituting (2) in (1), the layer thickness is expressed as a function of HT time and temperature:

$$y^2 = k_0(\exp(-E/\beta T))t\,. \tag{3}$$

Manuscript received August 5, 2002. This work was supported by the Department of Energy.

E. Barzi and S. Mattafirri are with the Fermi National Accelerator Laboratory, Batavia, IL 60510 USA (telephone: XXX-XXX-XXXX, e-mail: smattafirri@inwind.it). J.-M. Rey is from CEA Saclay, 91191 Gif sur Yvette Cedex, France. Fabio Fineschi is with University of Pisa, Italy.

By measuring the thickness of each intermetallic phase as a function of HT time and temperature, k_0 and E were evaluated using (3) for ε, η and δ phases, but only within the temperature ranges where the hypotheses for the applicability of the diffusion model are verified. Note that k, k_0 and E are empirical parameters for the intermetallic compounds. The latent period (t_0) needed for nucleation [2] had been at first included in the model and treated as a fitting parameter. It was later removed since its value resulted several orders of magnitude smaller than the HT durations.

III. Experimental Procedure

Diffusion samples were prepared by casting liquid Sn in Cu containers. Cu and Sn have been supplied by ex-IGC and are of the same quality than those used for superconductor manufacturing. Originally the casting of the Sn was performed by an oxyacetylene torch. However, this led to a non homogeneous interface between Sn and Cu. In order to improve temperature control and heat uniformity, the casting was then performed using a hot plate, which provided a very homogeneous Cu-Sn interface and allowed to substantially reduce the error on the thickness. Initially a bore of 11 mm in diameter was machined axially in Cu cylindrical bars and filled with tin (type A samples). After each HT step, a transverse slice of this rod was removed using a slow rotary saw, and then polished. After observing that the η phase growing in the liquid Sn could separate from the interface and either fall in the liquid Sn or float in it, the samples were modified. The copper bars were drilled transversally with several holes 5 mm in diameter, and 15 mm in depth, and filled with Sn (type B samples). After each HT step, a transverse slice that included a Sn filled hole was removed, and cut in two halves in the middle of the hole. HTs were conducted in a small furnace, with the diffusion samples sealed in pyrex tubes with nitrogen coverage. The samples in their sealed tubes were introduced in a pre-heated furnace. At the end of reaction, they were removed from the furnace and allowed to cool down at room temperature. Since the Sn was in liquid form in most of the samples, quenching the samples in cold water was not feasible. Table I shows the HTs performed.

Thickness measurements were performed using a Nikon optical microscope and Spot software. The surface area of the intermetallic layers was measured and divided by the length of the interface to determine the mean thickness of the layer. The measurement was repeated in four locations for each sample. This provides the mean thickness over a length of at least 400μm. For each phase and HT, the standard deviation on the avarage thickness gives a measure of the statistical error due to the natural fluctuations of the intermetallic growth, the instrumental errors and errors related to the operator. This error ranged from less than 1% to less than 20%, with typical values around 10%. The error related to the manufacturing procedure of the samples was evaluated using 16 additional samples for each casting procedure and sample geometry. The error related to the use of the hot plate and type B sample resulted 1.71% the thickness; the one related to the oxyacetylene torch and type B sample 7.82%; the one related to the oxyacetylene torch and type A sample 7.72%.

TABLE I
HEAT TREATMENTS

Cu-Sn Phase	T [°C]	Duration [h]
ε and η	400	3, 6, 12, 24, 48
	340	3, 6, 15, 24, 48
	240	3, 6, 12, 24, 78
	210	24, 48, 72, 100, 168
	180	24.5, 48.7, 88, 107, 155
	150	24, 48, 96, 144, 216
δ	550	5, 24, 48.8, 96.3, 136.5
	500	3, 6.3, 12, 24, 49, 88.5, 129, 179, 217, 273
	440	3, 6, 12, 24, 49.2, 91.2, 136
	400	3, 6, 12, 24, 48

The systematic errors on the thickness were also evaluated [3]. The major source of systematic error was identified in the HT cooling and heating transients of the samples. Since the duration of the HT is measured from sample insertion to its removal from the furnace, both the cooling of the sample to room temperature and the heating process lead to a systematic error. This error, evaluated for each HT, resulted at least two orders of magnitude inferior to the statistical one.

HTs are listed in Table I. The ε and η phase growth at 150, 210, 240, 340 and 400 °C, was already presented [4], and that the rate of growth at these temperatures of both η and ε phases and the E of ε phase, were published. The η and ε phase growth kinetics at the above temperatures is presented in this work in addition to the new temperatures investigated since the thickness data have been fitted with a more accurate method in order to estimate the diffusions constants and an accurate new error analysis has been performed on all the data.

IV. Kinetics of Growth in Cu/Sn Model Samples

Fig. 1 shows the thickness evolution of ε phase as a function of HT duration at the various temperatures within the thermal range of solid diffusion. Similar data have been obtained from 150 to 210°C for the solid diffusion of η phase. It can be seen that the diffusion of Sn in Cu is more effective after the melting of the Sn. The growth of the η and ε phases is low at 150, 180 and 210°C, and is of the same order of magnitude for the two phases.

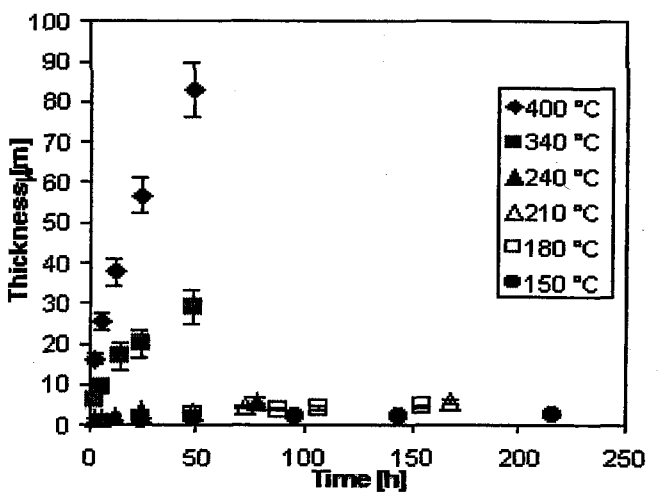

Fig. 1. Epsilon phase thickness as a function of HT duration at different HT temperatures.

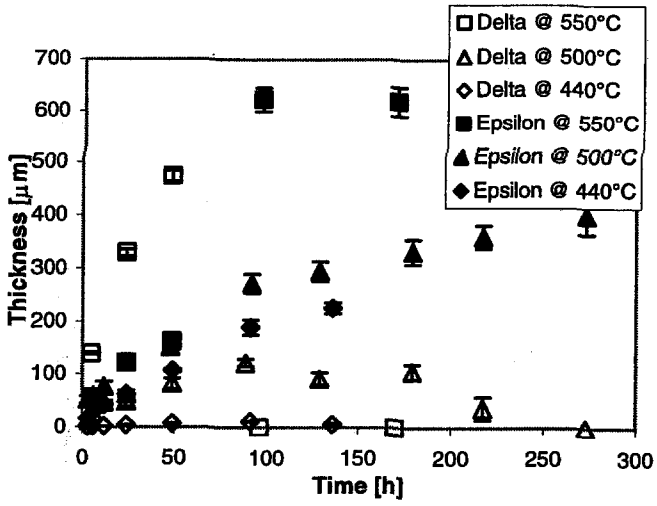

Fig. 2. Delta and epsilon phase thickness as a function of HT duration at different HT temperatures.

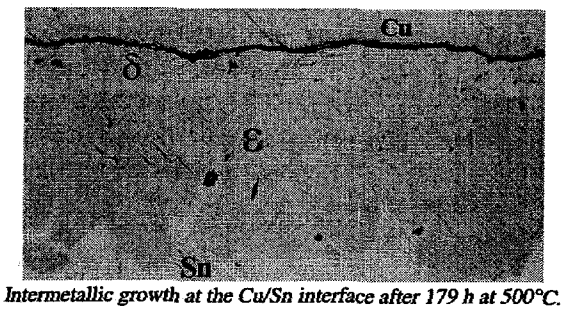

Fig. 3. Intermetallic growth at the Cu/Sn interface after 179 h at 500°C.

The δ phase thickness as a function of HT time and temperature is compared with ε growth in Fig. 2. One can see how at some point the ε phase starts growing at the expense of the δ phase until exhaustion of the latter. Fig. 3 shows the intermetallic growth after 179 h at 500 °C. It can be observed that the voids migration towards the higher melting compounds leads to a crack. This phenomenon has been observed at all investigated temperatures above 400 °C. After the continuous crack has formed, δ phase begins shrinking *while ε phase keeps growing until the exhaustion of δ phase.*

For each phase within the temperature ranges of solid diffusion, the activation energy (E) and diffusion frequency (k_0)

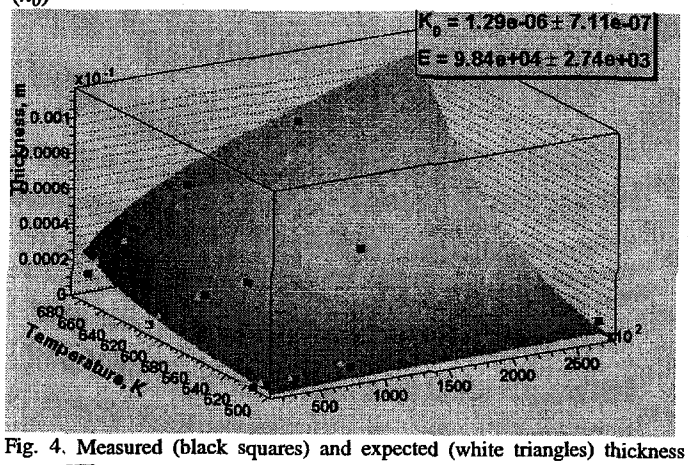

Fig. 4. Measured (black squares) and expected (white triangles) thickness versus HT parameters.

have been evaluated by a global χ^2 fit of the thickness data versus HT time and temperature using the parabolic growth law. An example of measured and expected thickness is illustrated in Fig. 4, and the results are shown in Table II. The values around 1 of the reduced χ^2 show that the parabolic growth model provides a good description of the observed distribution of data and that the errors have been accurately estimated. The diffusion constants of η phase developing into the liquid Sn were not evaluated since the η thickness evolution does not follow the parabolic growth law after the melting of the Sn [4].

TABLE II
DIFFUSION CONSTANTS

Cu-Sn Phase	T range [°C]	E [KJ/mol]	k_0 [cm²/s]	Reduced χ^2
η	150 - 227	102 ± 5.94	$2.12\ 10^{-5} \pm 3.35\ 10^{-5}$	1.08
ε	150 - 227	50.7 ± 3.59	$2.22\ 10^{-11} \pm 2.13\ 10^{-11}$	1.45
ε	227 - 415	98.4 ± 2.74	$1.29\ 10^{-6} \pm 7.11\ 10^{-7}$	0.93
δ	350 - 582	412 ± 10.9	$2.22\ 10^{14} \pm 3.82\ 10^{14}$	1.05

V. KINETICS OF GROWTH IN IT AND MJR STRANDS

The growth kinetics of η and ε phases was measured at 210, 240, 340 and 400°C in IT and MJR strands, whose design parameters are listed in Table III. Figure 5 shows the IT cross section at 210 °C after 1 week and at 400°C after 2 days. It can be observed that most of the Sn is still unreacted after 1 week at 210°C. It is worthwhile to mention that no wire burst or Sn leaks have been observed in the virgin strands for all the applied HTs.

Fig. 6 shows the ε and η growth comparison between the

TABLE III
STRAND PARAMETERS

Parameter	IT Strand	MJR Strand
Strand diameter [mm]	*1 ± 0.001*	*1.001 ± 0.001*
J_c (12 T, 4.2 K) [A/mm²]	700	2000
Filament size [μm]	5	3
Cu fr. %	58.7 ± 0.3	48 ± 0.3
Sn at. %	10.1	16
Nb at. %	20.4	50
RRR	300	20
Twist pitch [mm/turn]	25 ± 10	13 ± 3

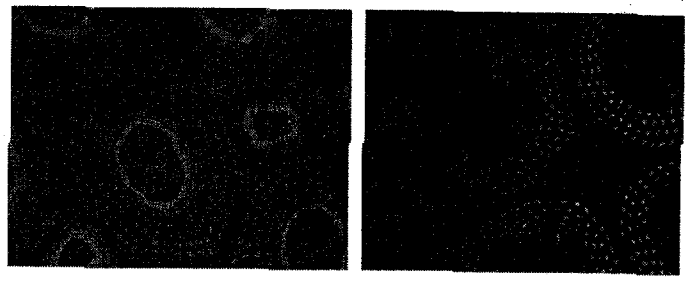

Fig. 5. Intermetallic growth in the IT strand: a) after 7 days at 210°C; b) after 2 days at 400°C.

IT and Cu/Sn model samples at 400°C. For all temperatures investigated and for both IT and MJR strands, it was observed that before depletion of the Sn, the ε phase growth in the strands is substantially the same as in the Cu/Sn model samples since the thickness difference is less than the statistical error on the measurement. After exhaustion of the Sn, the η phase supplies the Sn for the ε phase growth, and when also the η phase is depleted, the ε pool has been observed to shrink slowly due to formation of α phase. The η phase growth in the IT strand is in general different from that observed in the Cu-Sn models. This can be related to the depletion of the Sn, to the residual stress concentrations induced during wire manufacturing, to the presence of the filaments and to the non planar geometry of the Cu-Sn interface.

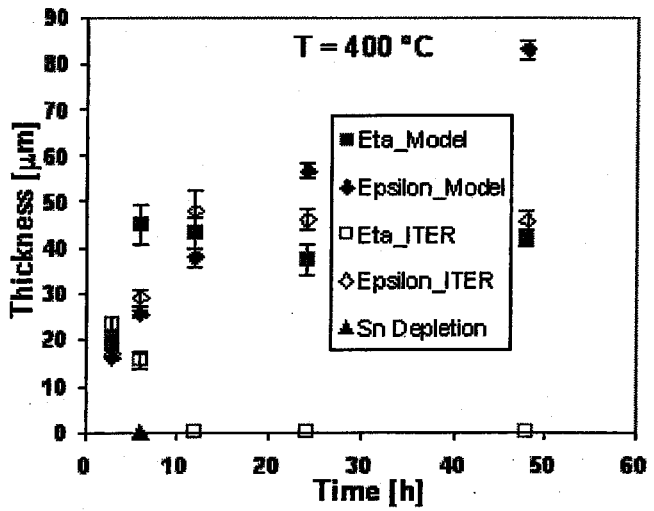

Fig. 6. Eta and epsilon phase thickness as a function of HT duration at 400°C in the Cu/Sn model samples and in the IT strand.

VI. Discussion

The results of the thickness growth investigation in IT and MJR strands show that before depletion of the Sn, the average thickness of ε phase is consistent with that formed in the Cu-Sn sample models. Therefore, the evaluation of the E and k_0 obtained with the sample models for the η, ε, and δ phases allows predicting the intermetallic thickness as a function of the HT parameters. This can be calculated for either a constant or a variable HT temperature, *i.e.* during temperature dwells or HT ramps.

The main objective of the HT low temperature steps in Nb_3Sn is Sn diffusion through the Cu. The investigation of the kinetics of phase growth shows that for temperatures above 440°C, the δ phase growth is associated with the formation of voids and segregations that may result in cracks along the diffusion path. Since this phenomenon hinders the diffusion process between Cu and Sn, the low temperature HT performed over the composite wires to diffuse the Sn in the Cu matrix should not be performed above 440 °C.

In addition to diffusing the Sn into the Cu, the low temperature steps of the HT should be programmed to also prevent leakage of Sn rich liquid phases, which has become an issue for high J_c Nb_3Sn strands. Whereas no wire burst or Sn leakage is typically observed in virgin strands, this is not true for magnets [5] or cables [6]. The only way to prevent leaks of Sn rich phases, which are characterized by low melting points, is to convert them into higher melting point phases. The results of the study on the strands show that a complete transformation of pure Sn into a higher melting point phase takes a very long time at temperatures below the melting point of the Sn. After 1 week at 210°C, which is a low temperature step often suggested by manufacturers to remove liquid phases, a large fraction of the Sn is still unreacted. Instead, the Sn and the η phase can be converted into the higher melting point ε phase and some traces of α phase substantially faster at 400°C. At such temperature, less than a day is adequate for total conversion without the liquid phases reaching the filaments. However, crossing the Sn melting temperature during a direct ramp to 400°C is sufficient to create Sn leakages in cables. In order to prevent this, temperature dwells below 227°C allow formation of an ε phase thin layer that may work as a container against the overpressure of the liquid Sn above 227°C. Since the ε phase thickness formed at 210°C after 1 week is only about 1 μm larger than that formed after 3 days, a 3 day 210°C dwell followed by a 1 day at 400°C should not only appropriately diffuse the Sn through the Cu, but also prevent Sn leaks, as experimentally confirmed on cables in [6].

In typical strands, the Sn cannot be uniformly and homogeneously distributed around all the Nb filaments prior to the beginning of the A15 phase formation. The inner ring of the Nb filaments is immersed into ε phase, while the outer ring is immersed in α phase and/or pure Cu. However, it is not yet clear to what extent matrix heterogeneity influences Nb-Sn diffusion.

VII. Conclusions

The diffusion constants of ε, η and δ phase were evaluated within their temperature ranges of solid diffusion. Applicability of the parabolic growth law model to IT and MJR strands to describe ε phase growth was proved. This allows programming the low temperature steps of the HT for different strands designs, either for a constant or variable HT temperature. Moreover, an upper limit of 440°C to long temperature dwells has been identified.

References

[1] Handbook

[2] "Intermetallic Compounds. Principles and Practice", vol 1, Ed. J.H. Westbrook and R.L. Fleischer, 1994.

[3] S. Mattafirri, "Kinetics of phase growth during the Cu-Sn diffusion process and the Nb3Sn formation. Optimization of superconducting properties",Technical Division TD-02-021, Fermilab, May 2002.

[4] J. M. Rey, E. Barzi, S. Mattafirri, J. Hoffman, R. Yamada, "Effect of Partly Reacting Nb_3Sn before Magnet Winding on the Strand Critical Current", CEC/ICMC, 2001.

[5] D. R. Chichili, N. Andreev, E. Barzi, V.V. Kashikhin, I. Terechkine, S. Yadav, R. Yamada, and A. V. Zlobin, "Nb_3Sn Cos(θ) Dipole Magnet, HFDA-02 Production Report", Technical Division TD-01-036 Fermilab, May 2001.

[6] E. Barzi and C. Boffo "Effects of Long Heat Treatments on the Properties of Nb3Sn composites Strands", this Conference Proceedings.