

The Interdiffusion of Cu and Sn in Internal Sn Nb₃Sn Superconductors

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Abstract—For Nb₃Sn superconductors manufactured by the internal Sn process, the most appropriate heat treatment is still a matter of debate. The major complications are the low melting temperature of Sn and the 7 Cu–Sn phases. Each phase has its own diffusivity and atomic volume, which differs significantly from the pure Sn and Cu phases from which the diffusion starts. Void formation near the Nb filaments, due to the presence of high-Sn phases, complicates both the reaction kinetics and thermodynamics, often introducing local non-uniformity. To try to understand these problems better, 24 hour heat treatments approximately 10° C above and below the Cu–Sn invariant temperatures have been performed on a Nb₃Sn ITER strand. The pure Sn core was replaced by η-phase bronze after 24 hours at 237° C. After 24 hours at 401° C, the η-phase itself was completely replaced by ε-phase. It appears that γ-phase undergoes a eutectoid reaction, breaking down into α and δ phases. Mg initially in the Sn core was only found in a Cu–Sn–Mg ternary at all heat treatment temperatures.

INTRODUCTION

The higher critical current density of internal Sn Nb₃Sn wires compared to those made by the bronze process makes them the preferred choice for conductors for the next generation of high field magnets. A problem inherent in all internal Sn designs is the need to diffuse the Sn from a central reservoir or core through the Cu matrix to the Nb filaments. In the Cu–Sn binary alloy system (Fig. 1), there are 6 intermetallic phases between Sn and Cu. All heat treatment schedules perform a diffusion heat treatment step prior to the Nb₃Sn reaction in an effort to homogenize the Sn around each filament. Lack of full homogenization is common which leads to less than optimum properties. The extent and nature of the compromise produced by this inhomogeneity is unclear because each Nb₃Sn filament forms under different local conditions.

There is as yet little clear guidance on what the optimum homogenization reaction for internal Sn conductors should be. A general concern about the presence of liquid phases bounds many heat treatment (HT) schedules. Primary in this concern is what happens when Sn melts, but two of the seven Cu–Sn phases (γ and η) also have melting points at or below typical Nb₃Sn reaction temperatures (600° - 700° C). However, it is the low melting point of the η-phase (415° C) and that of the pure Sn (232° C) that are generally of most concern in the Sn homogenization process. For example, if heat treatments are performed above the η-phase melting point, it is not unreasonable to suspect that the inner ring of Nb fila-

ments becomes immersed in ε and liquid phases and moves, allowing contact with adjacent filaments and thus increasing hysteresis losses. This implies that a significant portion of the Cu–Sn homogenization should occur below 415° C until all of the η-phase is converted into higher melting point phases.

Another complex issue is that of void formation, which is very common in internal Sn wires. The cause of the voids appears to be due to atomic density and diffusion coefficient differences between the different phases [2]. Agglomerated voids may have a number of deleterious effects. They hinder the interdiffusion of Cu and Sn and, when in contact with a Nb₃Sn filament, voids may introduce stress concentrations that decrease the superconducting parameters. A heat treatment protocol that minimizes or eliminates void formation is generally agreed to be highly desirable.

As a first step to understanding the Sn homogenization step, we have performed heat treatments on an ITER-type internal Sn conductor and have examined the phases present after heat treatment, just below and just above each invariant in the Cu–Sn phase diagram.

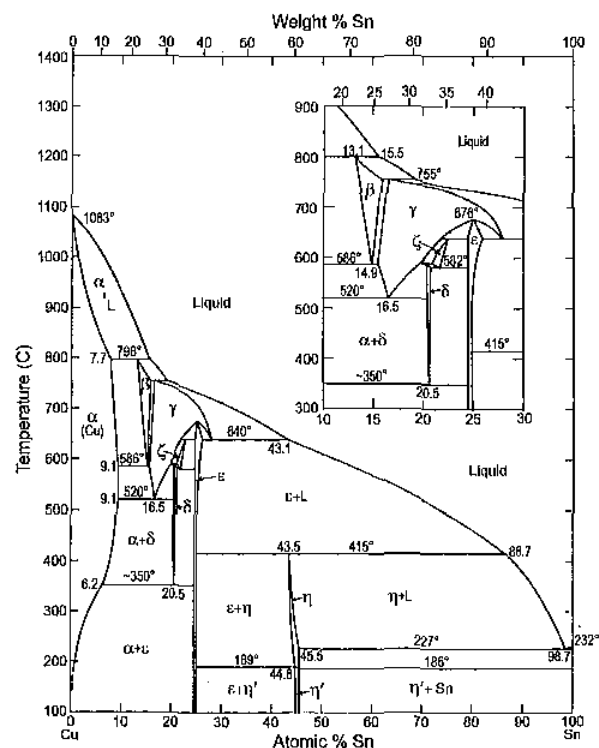


Fig. 1. The Cu–Sn phase diagram adapted from [1].

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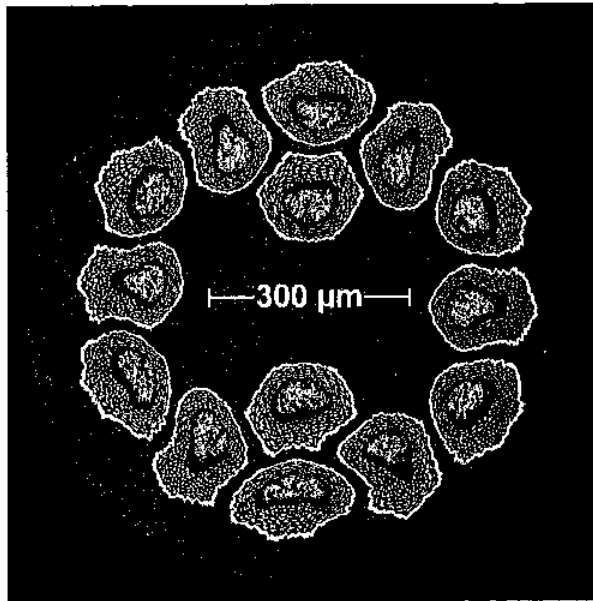


Fig. 2. The wire cross section prior to heat treatment.

EXPERIMENTAL PROCEDURE

ITER wire, designed for the HPI intermediate hysteresis loss with high J_c specification, manufactured by Oremet Wah Chang (formerly Teledyne Wah Chang) was provided for the study. The strand was made by the modified jelly roll process [3]. It consisted of 14 bundles of a Sn-Mg core surrounded by a double-wrap of Cu and Nb-1wt.%Ti expanded metal filaments, all surrounded by a Ta-40wt.%Nb diffusion barrier (Fig. 2 and 3). The overall Cu-Sn composition was calculated to be Cu-13at.%Sn by image analysis. This is higher than the Cu-10at.%Sn calculated using the component areas given by Glowacki [4]. Both calculations, however, place the overall composition at just greater than the α -phase solid solution (9.1at.% Sn). The wires were heat treated at temperatures approximately 10°C above and below the in-

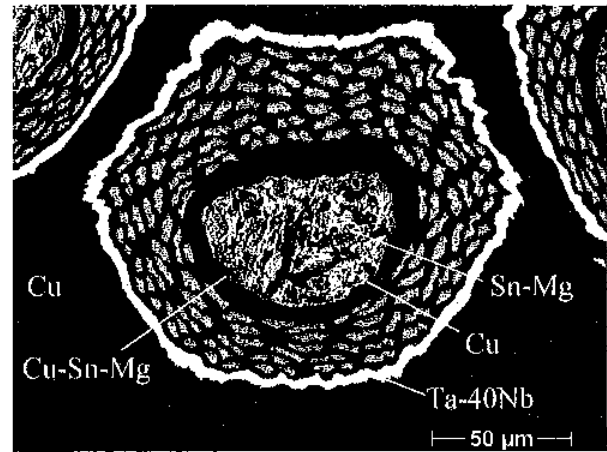


Fig. 3. An individual bundle prior to heat treatment. A 1 to 3 μm thick layer of η -phase can be seen around the Sn-Mg core.

variant temperatures of the Cu-Sn binary alloy system. One of the problems with heat treating short samples of internal Sn wires is effective sealing of the ends. Usually, the wire ends are crimped, but liquid Sn still often leaks out. To avoid such leakage, we electroplated ~ 1 mm of Cu onto the wire ends. No leaks were detected upon examination after heat treatment. After electroplating, the wires were sealed in quartz tubes under an argon atmosphere of ~ 20 mTorr and inserted directly into a furnace for 24 hours. At the end of the heat treatment, the tubes were quenched in water to retain any phases formed during heat treatment. Phases were determined by light microscopy, electron dispersive spectroscopy (EDS) and backscatter electron (BSE) images, which were taken in a JEOL JSM-6100 Scanning Electron Microscope (SEM).

RESULTS

Atomic-number-sensitive, BSE images after each heat treatment are shown in Figure 4 and the phases found are compiled in Table I. Below the eutectic of Sn and η there

TABLE I
HEAT TREATMENT RESULTS

Heat Treatment Temperature	Cu-Sn Bronze Phases Detected							Pure Sn	Mg-Cu-Sn Ternary
	α	β	γ	δ	ζ	ϵ	η		
218 $^\circ\text{C}$	✓							✓	✓
237 $^\circ\text{C}$	✓							✓	✓
335 $^\circ\text{C}$	✓							✓	✓
360 $^\circ\text{C}$	✓							✓	✓
401 $^\circ\text{C}$	✓			✓				✓	✓
426 $^\circ\text{C}$	✓			✓				✓	✓
510 $^\circ\text{C}$	✓			✓				✓	✓
528 $^\circ\text{C}$	✓		✓*					✓	✓
569 $^\circ\text{C}$	✓		✓*					✓	✓
599 $^\circ\text{C}$	✓	✦	✦					✓	✓

* -- Underwent a eutectoid reaction upon cooling, breaking down into a refined microstructure of δ and α .

✦ -- Believed to have been the phases originating the fine scale microstructure seen after quenching.

Shaded areas represent heat treatment temperatures where a given phase is not stable according to Fig. 1.

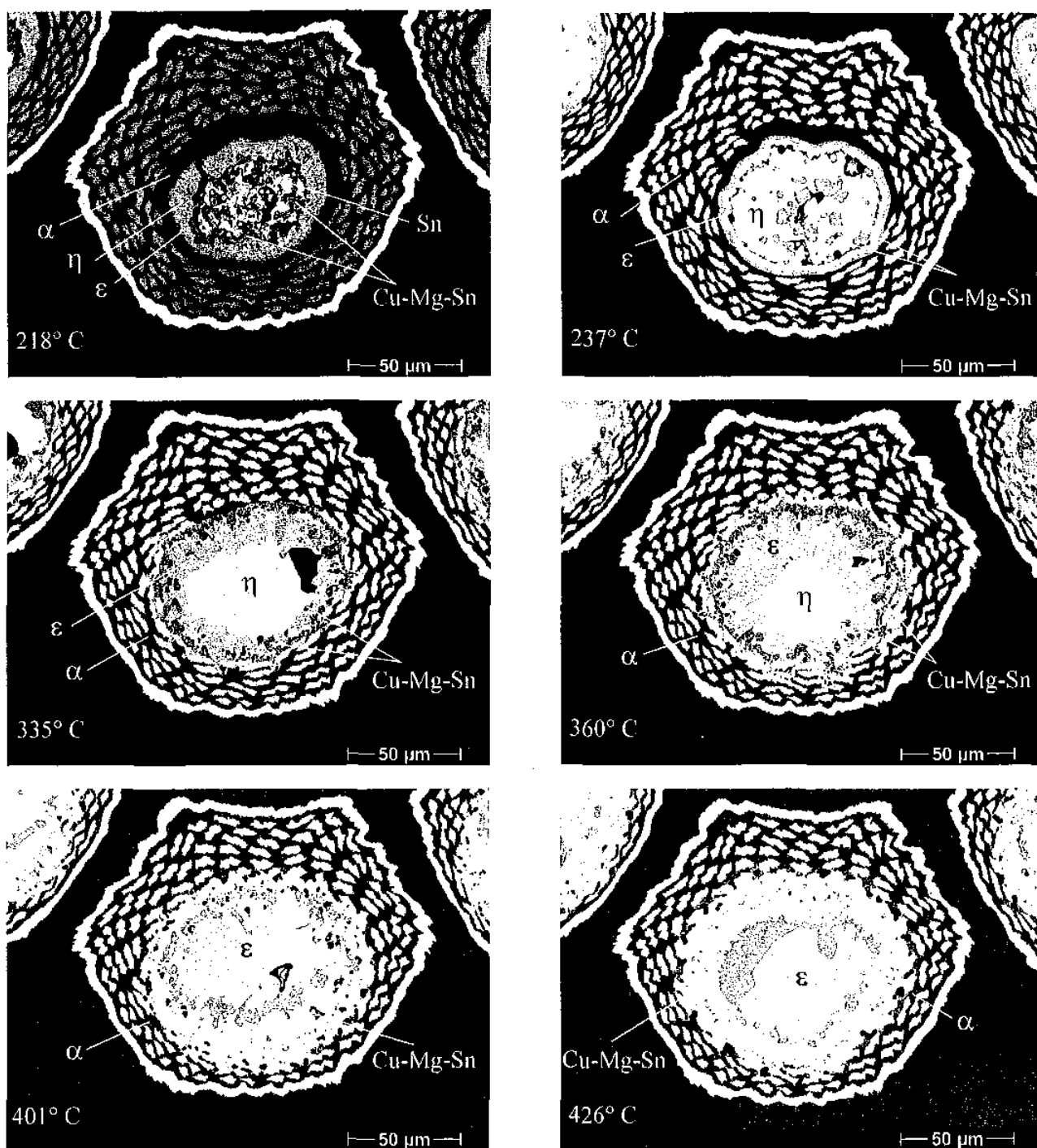


Fig. 4. SEM-BSE images at the same magnification and of the same bundle showing the effects of 24 hour heat treatments at 218° C, 237° C, 335° C, 360° C, 401° C and 426° C.

was some reaction to η and ϵ , but some unreacted Sn remained after 24 hours at 218° C. This residual Sn did dissolve after 24 hours at 237° C, 10° C above the eutectic.

For the 237° C, 335° C and 360° C heat treatments, the ϵ -phase expanded both toward the filaments and, at the expense

of the η -phase, toward the core. The η -phase for the most symmetric bundles (those shown) did not reach the filament rows, but did in some of the asymmetric bundles heated at 237° C and 335° C. Where η -phase came in contact with a filament, there was a noticeable lack of ϵ -phase formation.

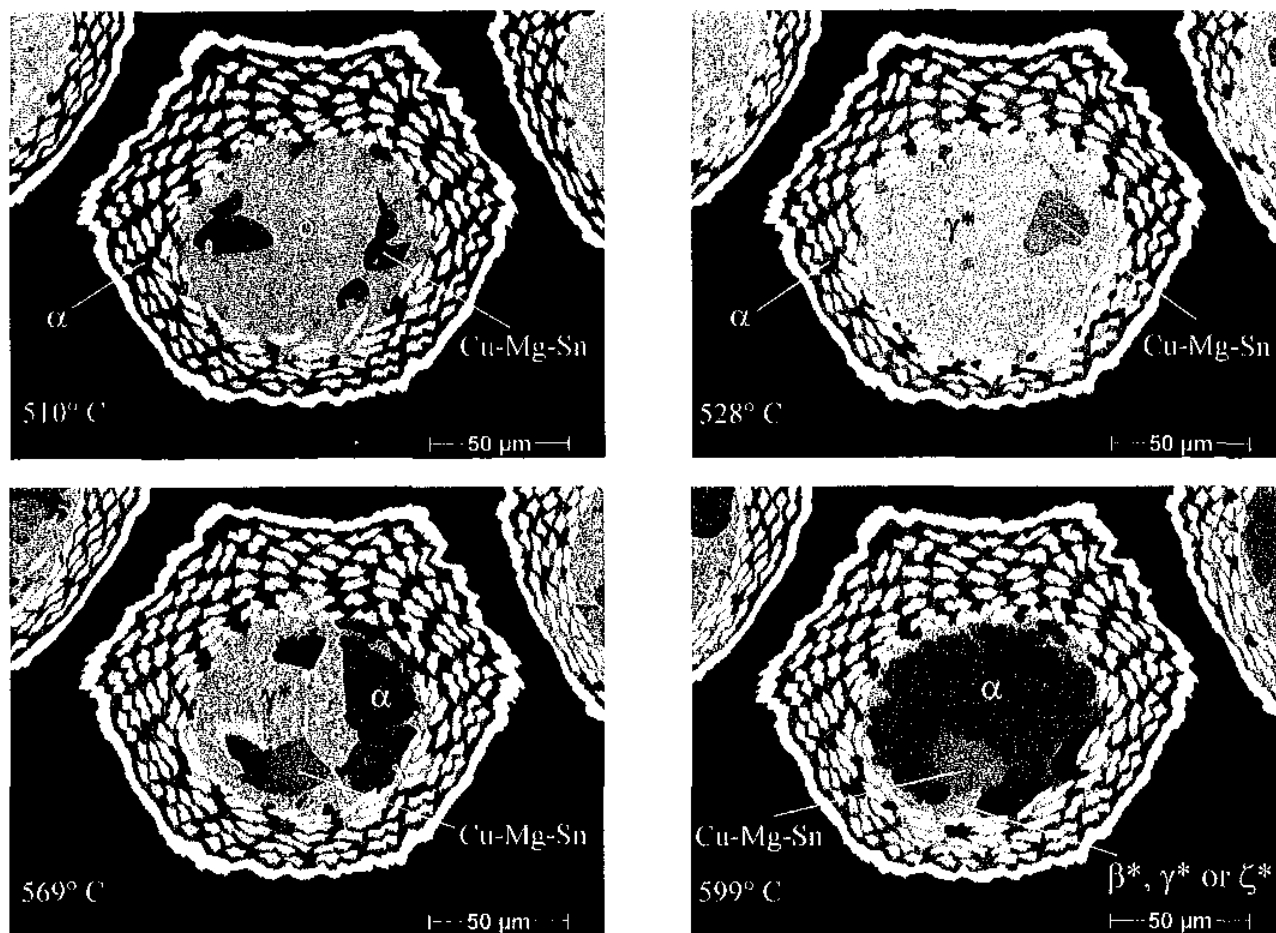


Fig. 4. (continued) SEM-BSE images at the same magnification and of the same bundle showing the effects of 24 hour heat treatments at 510° C, 528° C, 569° C and 599° C. Phases with * underwent a eutectoid decomposition.

After 24 hours at 401° C, the η -phase had been completely replaced by ϵ -phase.

Although predicted by the phase diagram, δ -phase was not seen at 360° C. Interestingly, there was no contrast in the BSE image between δ and ϵ phases, and we had to rely on light microscopy and EDS for identification. In the 528° C, 569° C and 599° C heat treatments, a refined microstructure suggestive of a eutectoid decomposition was seen. A furnace cooled sample heat treated for 24 hours at 530° C showed a coarsened microstructure, suggesting that an $\alpha+\epsilon$ mixture was produced from the δ -phase breakdown.

A distinct ring of small voids was seen in the η -phase at 218° C even in the solid state, becoming even more pronounced at 237° C. At 335° C and 360° C, there was a band of voids, which remained within the high-Sn phases. At higher temperatures, the voids coarsened and formed a distinct ring within the first few rows of filaments. Larger voids were seen in the central portions of at least a few bundles of each wire (similar to that of the 335° C heat treatment) for all except the 510° C heat treatment.

Filament movement was apparent in the heat treatments above 360° C. At 401° and 426° C, there was an increase in filament separation for filaments lying within the ϵ -phase. However, the filament separation decreased for the inner rows of filaments at 569° and 599° C. There appear to be both increases and decreases in the filament separation after the 510° C and 528° C heat treatments.

The Mg that was put into the Sn core was found to be captured within a Cu-Sn-Mg ternary for all heat treatment temperatures. A correlation was seen between the heat treatment temperature, the composition and the shape of the Cu-Sn-Mg ternary. The composition of the Mg ternary changed from approximately Cu-29at.%Sn-36at.%Mg after 24 hours at 218° C to Cu-15at.%Sn-15at.%Mg for the 510° C, 528° C, 569° C, and 599° C heat treatments. The ternary formed individual particles within the core region after the 218° C and 237° C heat treatments. As the heat treatment temperature increased, the Cu-Sn-Mg ternary moved to the periphery of the core region, forming of a broken ring of particles (335° C and 360° C). At 401° C and above, the Mg ternary coalesced into large particles, and eventually formed just one particle

(569° C and 599° C). If there was Mg in the Cu–Sn bronze phases examined, the level was too low to be found accurately by EDS without extremely long analysis times.

Summarizing our findings, we observed that the voids moved radially outwards with the Cu–Sn intermetallic phases (i.e. non α -phase) and remained at the maximum penetration of these phases' into the filaments

DISCUSSION

Based on the results of this experiment, an effective first heat treatment step may be at 360° C. This would avoid η -phase melting and minimize filament motion. Obviously, the hold time should be longer than 24 hours in order to dissolve the η -phase, but the exact time is yet to be determined. Although 401° C is also below the η -phase melting point, filament motion is evident. Because this is likely to lead to increased hysteresis loss, it is to be avoided. Many industrial heat treatments have long hold times below the Sn melting point (232° C). An anecdotal reason for this is to avoid blow out of Sn at weak points in the wire, a not uncommon effect 10 years ago. Whether this is really needed in modern wires is not clear from the literature. Experiments by Dietderich et al. [5] on a different strand suggested that it is possible to avoid the low temperature anneal and get an equivalent microstructure and J_c .

We expected that δ -phase would form above 350° C, especially between the ϵ - α interfaces, however it was not seen at 360° C. In a subsequent experiment, δ -phase was also not seen after 150 hours at 362° C. A lack of δ -phase formation has been observed by Onishi et al. [6] after 39 hours at 404° C. Verhoeven et al. [7] also noted a lack of δ -phase after 20 days at 200° C followed by 6 hours at 400° C. They did, however, see δ formation after 20 days at 200° C followed by 88 hours at 400° C. A difference between the previous two references and this experiment, however, was that they were examining Sn-plated Cu sheet.

Faster heating rates minimize filament motion at the expense of worsening Sn homogeneity within the bundle [8]. This suggests that the filament motion observed here during isothermal heat treatments is minimized. We believe that it is unlikely that the cause of filament motion was immersion in any liquid phase. This is because η -phase, the lowest melting point Cu–Sn phase, never reached the filaments and the heat treatment temperatures are below the melting points of the other phases.

Another cause of filament motion is the volumetric expansion of the surrounding phases. At 401° and 426° C, there was an increase in the filament separation for the filaments within the ϵ -phase. This might be due to the lower atomic

density of the ϵ -phase compared to that of the α -phase. Countering this, however, is the fact that the filament separation decreased for the inner rows of filaments at 569° and 599° C. The other possible non- α phases at these temperatures (δ and γ) have a similar atomic density to that of ϵ phase, so one might expect to see a similar filament expansion. Moreover, there does not appear to be any motion after 24 hours at 360° C and many of these inner filaments are surrounded by ϵ -phase too.

The fine scale microstructure of the 528° C and 569° C heat treatments can best be correlated with γ -phase that has undergone a eutectoid decomposition during cooling. This is corroborated by a furnace-cooled sample that consisted of a coarse α and δ mixture. The refined microstructure of the 599° C heat treatment could also include eutectoid decompositions of β or ζ phases, as those phases are also stable at this temperature.

CONCLUSIONS

ITER type internal Sn Nb₃Sn strand was heat treated above and below the temperature invariants of the Cu–Sn binary system. It is believed that filament motion is minimized and η -phase melting is avoided by heat treating at 360° C. Voids move outward with the α -phase boundary and stop at the furthest extent of the high Sn phases. δ -phase first formed only after 24 hours at 510° C, even though predicted to form above 350° C.

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