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The crystal structure of $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ in the Cu-Nb-Sn system

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ABSTRACT

During the processing of superconducting Nb_3Sn wire, several intermediate intermetallic phases including a previously encountered Cu-Nb-Sn phase show up. The yet unknown crystal structure of this phase is now identified by a combination of different experimental techniques and database search to be of the hexagonal NiMg_2 type with a proposed composition of about $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$. The structure determination started from an evaluation of the lattice parameters from EBSD Kikuchi patterns from quenched material suggesting hexagonal or orthorhombic symmetry. A database search then led to the hexagonal NiMg_2 type structure, the presence of which was confirmed by a Rietveld analysis on the basis of high energy synchrotron X-ray powder diffraction data. Assuming a partial substitution of Nb in orthorhombic NbSn_2 by Cu, the change of the valence electron concentration provokes a structural transformation from the CuMg_2 type for NbSn_2 to the NiMg_2 type for $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$. In the previous literature the $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ phase described here has occasionally been referred to as Nausite.

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1. Introduction

The intermetallic superconducting phase Nb_3Sn plays a very important role in superconducting magnets, e.g. those presently built for the High Luminosity upgrade of the Large Hadron Collider (HL-LHC) at CERN [1,2,3]. During the production process using powder-in-tube technology (PIT) or the restack rod process (RRP), a diffusion heat treatment is employed that finally forms the Nb_3Sn phase with A15 type structure [4,5]. The particular PIT technology is based upon a reaction of the core containing NbSn_2 and β -Sn powder with a Cu sheath and the surrounding tube made of a Nb(Ta) solid solution [5,6].

During the diffusion heat treatment several reactions take place involving numerous intermetallic phases the compositions of which are illustrated in Fig. 1, beginning with the formation of η - Cu_6Sn_5 and ε - Cu_3Sn at the interface of the powder with the Cu sheath. At 408 °C η - Cu_6Sn_5 undergoes a peritectic decomposition into ε - Cu_3Sn and liquid Sn [7]. A ternary phase with until now unknown crystal structure is encountered in high-Sn-content Nb_3Sn wires upon heating above ~340 °C in microstructural investigations performed after the heat treatment (e.g. in Modified

Jellyroll (MJR) [5] Rod-In-Tube (RIT) [8], PIT [9] and RRP [10] and in *in-situ* diffraction experiments [4,10,11]. In PIT wires at ~575 °C the ternary compound disappears followed by a reappearance of the NbSn_2 phase and a fcc Cu-based solid solution containing up to 9.5 at% of Sn (α bronze) [10]. Through the dissolution of the copper sheath, the NbSn_2 phase reacts with the outer Nb tube forming Nb_6Sn_5 . The desired fine-grained Nb_3Sn is formed by solid-state diffusion of Sn into the Nb(Ta) tube, whereas large grained and poorly connected Nb_3Sn is formed directly from Nb_6Sn_5 [12]. The strongly different Nb_3Sn microstructures across the Nb_3Sn layer limits the wire overall critical current [13].

The ternary phase, which is sometimes called Nausite [8,13] because it was first observed by Naus [5], is typically encountered as sub-micrometre layer at the interface between the former Cu sheath [9] of the PIT wire and at the middle as well as on the edge of the core of the RRP samples [14]. During heating experiments on wires monitored by synchrotron X-ray diffraction (XRD), the ternary phase was observed between 350 °C and 580 °C [15]. Several compositions of the ternary phase were reported from energy dispersive x-ray spectroscopy (EDS) measurements in a scanning electron microscope (SEM) [14,16,17]. However, the EDS results are likely affected by the small size (<500 nm) of the homogenous phase regions, being smaller than the interaction volume of the electron probe. Most accurate measurements are obtained by EDS measurements in a transmission electron

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Fig. 1. Concentration triangle indicating the compositions of the various intermetallics encountered during the Nb₃Sn PIT wire processing including the ternary (Nb_{0.75}Cu_{0.25})Sn₂ phase analysed in the present work.

microscope (TEM) revealing a composition of 66 at% Sn, 25 at% Nb and 8 at% Cu without that Ta was detected [9]. This observed composition implies that one quarter of the Nb atoms in the compound NbSn₂ was substituted by Cu. None of the currently known phase diagrams of Cu-Nb-Sn contains a ternary phase, but solid solutions of binary intermetallic phases with a third element can be found, e.g. up to 5 at% for Cu in NbSn₂, Nb₆Sn₅ or Nb₃Sn [18].

In the present work a structure model for the (Nb_{0.75}Cu_{0.25})Sn₂ phase is derived from lattice parameters and the Bravais lattice on the basis of the analysis of electron backscattered diffraction (EBSD) Kikuchi patterns [19] and an educated guess based search in crystallographic databases. This yielded the NiMg₂ type structure (space group *P6₂22*), which is also encountered in other transition metal distannides of similar valence electron concentration. The structure model was confirmed by analysis of synchrotron X-ray diffraction (XRD) data. Moreover, EBSD analysis using the derived structure revealed insight into the characteristic microstructure of the ternary phase evolving during the PIT process.

Fig. 2. Schematic structure of one individual filament of a Nb₃Sn composite wire before the heat treatment: NbSn₂ and Sn powder are enclosed by a hexagonal Nb(Ta) tube, which is lined inside with a Cu sheath; the surrounding Cu matrix interconnects the individual filaments within the wire.

2. Experimental

For the present study an Nb₃Sn PIT wire was selected because it is the wire type in which a comparatively large amount of the ternary phase is formed during processing [15]. The PIT wire produced by Shape Metal Innovation (now Bruker EAS) [6] has a nominal diameter of 1.25 mm, a Cu to non-Cu volume ratio of 1.22, and it contains 288 hexagonal filaments within a Cu matrix. The filaments with an effective diameter of 50 μm consist of a precursor powder core of NbSn₂ + Sn inside a thin Cu sheath, which is surrounded by a Nb(7.5 wt% Ta) tube (Fig. 2). Previous experiments [4] had shown that in this PIT wire the maximum amount of the unknown ternary phase is formed during the reaction heat treatment at 480 °C. Therefore, the EBSD experiments have been performed with identical PIT wire samples that were heated with a temperature ramp of 60 K/h up to a peak temperature of 480 °C, and subsequently quenched in air.

For SEM experiments the heat-treated sample was embedded, then ground and polished in transverse cross-section with a final polishing by colloidal silica (Bühler Vibromet) for 6 h. More details about the polishing procedure that enables indexing of crystallites as small as 100 nm can be found in Ref. [20]. The EBSD/EDX investigations were performed on a FEG-SEM LEO 1530 using an electron energy of 20 keV. The applied 120 μm aperture enabled a beam current of about 7.5 nA. The collected EBSD patterns were processed using HKL Channel 5 (Oxford Instr.).

High-energy synchrotron XRD experiments were conducted at the beamline ID15A of the European Synchrotron (ESRF), Grenoble. The wires were measured in transmission with an energy of 88.005 keV of the X-rays under in-situ heating. Debye-Scherrer diffraction patterns were recorded using a 2D detector (MAR345) and integrated to 2θ diffraction patterns. A detailed description of the experiment and the full data are given in Ref. [4]. Multiphase Rietveld refinement on the basis of the full pattern obtained at room temperature subsequent to heat treatment with $T_{\max} = 480$ °C was conducted using the software TOPAS V5.0 [26]. The crystallographic description of the individual phases observed besides the ternary phase and the starting values for the refinement of the lattice parameters can be found in Table 1. Only the lattice parameters, the phase fractions, and one overall value for the atomic displacement parameter of these additional phases were refined. The fractional coordinates of all atomic positions were kept unchanged, except for the refineable coordinates of the Sn atoms of the (Nb_{0.75}Cu_{0.25})Sn₂ phase.

3. Results

The characteristic microstructure of the wire after the heat treatment up to 480 °C is shown in Fig. 3. The individual filaments embedded in the Cu matrix can be seen in Fig. 3a. A detailed view of a single filament is given in Fig. 3b. By the employed backscattering contrast, which is approximately related to the atomic number,

Table 1

Crystallographic description of the analysed phases and lattice parameters from the literature as used as starting parameters for the Rietveld refinement.

Phase	Cu ₆ Sn ₅	Cu ₃ Sn	NbSn ₂	Cu	Nb
Reference	[21]	[22]	[23]	[24]	[25]
Space group	<i>P6₃/mmc</i>	<i>Pmmn</i>	<i>Fddd</i>	<i>Fm3m</i>	<i>Im3m</i>
<i>a</i> [Å]	4.192	5.49	9.874	3.61	3.2941
<i>b</i> [Å]		4.32	5.626		
<i>c</i> [Å]	5.037 ^a	4.74	19.116		

^a For simplicity the disordered model for the Cu atoms in this phase was considered in the present evaluations.

Fig. 3. SEM characterisation of the sample after 480 °C heat treatment using backscattered electrons: a) wire overview, b) reaction layer of an individual filament, c) detailed view on the reaction layer at the former Cu sheath.

besides the dark outer Cu matrix and the Nb(Ta) hexagonal tube several characteristic areas can be identified. The former Cu sheath decomposed into a darker appearing region, which was identified as Cu_3Sn and a brighter fringe at the interface with the Nb(Ta) tube, which represents the unknown ternary phase [14]. The core of the filament exhibits a similar brightness as the outer ternary phase, suggesting that the initial precursor particles might also be transformed to the ternary phase as well. Further, several dark grains can be identified in the core, too, which might be ascribed to *fcc*-Cu or, due to the presence of Sn, to *fcc*-Cu-Sn solid solution (α bronze). To reveal the size and the shape of the reaction layer at the former Cu sheath a detailed image in Fig. 3c is shown, highlighting the ternary phase area between the Cu_3Sn layer and the nanocrystalline Nb(Ta) tube.

Combined EBSD/EDS measurements confirm the local phase microstructure (Fig. 4) of a vertical section of the reaction layer. The EBSD phase map (Fig. 4a) confirms the existence of Cu_3Sn (yellow), which was formed by the reaction of the Cu sheath with the Sn of the powder core. Obviously Cu_3Sn is produced from the liquid due to the peritectic decomposition of Cu_6Sn_5 above 410 °C. Thereby, homogeneous, uniform, coarse-grained crystallites are formed, which show nearly one single crystallographic orientation along the whole interface with the initial powder core. On the left side towards the powder core Cu_6Sn_5 (orange) was identified, which has probably re-formed during cooling off the sample [4]. The corresponding EDS data is visualised in Fig. 4b–d), confirming the

observed phase discrimination made by EBSD. The expected area of the ternary phase as well as the majority of the former powder core could not be indexed as Cu_6Sn_5 , Cu_3Sn , NbSn_2 , Cu or Nb, although the superimposed band contrast in Fig. 3a suggests well-pronounced EBSD Kikuchi patterns. Therefore, a single non-binned Kikuchi pattern (1343×1024 pixels) was investigated using EBSDL, a software which enables the determination of the Bravais lattice as well as the lattice parameters from a single EBSD Kikuchi pattern [19].

For the analysis of a single EBSD Kikuchi pattern (Fig. 5a) by using the EBSDL software, as many as possible bands are required described by their positions and widths. The solution of this over-determined system of equations is comparatively accurate since all band positions but also band widths within a pattern are strongly correlated. As additional information the approximate projection centre position (pattern centre and source-screen distance) is needed. In order to have suitable start values for the projection centre position a Cu pattern collected close to the position of the unknown phase has been applied, cf. Fig. 5b. For the lattice-parameter determination several patterns formed by the unknown phase have been checked. The occurrence of numerous unusually narrow bands with obviously higher indexing indicated that the unknown phase exhibits large unit cell dimensions (cf. Fig. 5a) as compared to *fcc*-copper (Fig. 5b).

The patterns are evidently incompatible with cubic symmetry due to missing symmetry elements. Instead, at the bottom left

Fig. 4. EBSD/EDS measurement of the reaction layer: a) band contrast and phase map with orange - Cu_6Sn_5 , yellow - Cu_3Sn , red - *fcc* Cu, blue - *bcc* Nb, not coloured areas are not indexed; qualitative EDS count maps with phase boundaries superimposed by black lines: b) Sn $L\alpha$, c) Cu $K\alpha$, d) Nb $L\alpha$. Due to different information depths of characteristic X-rays and Kikuchi pattern slight mismatches between the chemical and diffraction information are observed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Comparison of EBSD Kikuchi pattern of the a) unknown phase and b) Cu. The numerous and comparatively narrow bands of the unknown phase indicate a unit cell of clearly bigger dimension than that of Cu.

corner a single three-fold or six-fold symmetry axis seems to be present, speaking for a hexagonal or rhombohedral Bravais lattice or for pseudo-symmetric lower-symmetric lattices. For an extraction of the lattice parameters clearly visible band edges are necessary. Unfortunately, this is the case for a few bands only, which makes a definition of reliable reciprocal lattice vectors challenging. Nevertheless, using EBSDL two descriptions have been discovered with either a hexagonal unit cell ($a = 5.27 \text{ \AA}$ and $c = 13.08 \text{ \AA}$, $c/a = 2.49$), or an orthorhombic (but pseudo-hexagonal) unit cell with lattice parameters $a = 5.26 \text{ \AA}$, $b \approx 3^{1/2} a = 9.05 \text{ \AA}$, and $c = 13.03 \text{ \AA}$.

A database search [27] revealed that several transition metal distannides with hexagonal symmetry and comparable lattice parameters are known: MoSn_2 [23]; $\text{TiMnSn}_4 (= (\text{Ti}_{0.5}\text{Mn}_{0.5})\text{Sn}_2)$ [28]; $\text{Ti}_{0.4}\text{Fe}_{0.6}\text{Sn}_2$, $\text{Fe}_{0.4}\text{V}_{0.6}\text{Sn}_2 (= (\text{V}_{0.6}\text{Fe}_{0.4})\text{Sn}_2)$, $\text{Co}_{0.28}\text{V}_{0.72}\text{Sn}_2 (= (\text{V}_{0.72}\text{Co}_{0.28})\text{Sn}_2)$ [29] and $\text{NiCr}_5\text{Sn}_{12} (= (\text{Cr}_{0.83}\text{Ni}_{0.17})\text{Sn}_2)$ [30]. They are all described by the NiMg_2 structure type (space-group type $P6_322$, Strukturbericht notation C_a). There is a strong evidence that this structure type is also applicable for the unknown ternary

Table 2

Structure model of NiMg_2 -type $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ phase ($P6_322$) derived from a multi-phase Rietveld refinement on the basis of synchrotron XRD data recorded from a wire at room temperature after heating to 480°C .^{a,b}

Lattice parameters: $a = 5.647(9) \text{ \AA}$, $c = 14.130(5) \text{ \AA}$, $c/a = 2.502$					
Site	Wyckoff symbol	x	y	z	Occupation ^a
M(1)	3b	0	0	1/2	0.75 Nb/0.25 Cu
M(2)	3d	1/2	0	1/2	0.75 Nb/0.25 Cu
Sn(1)	6f	1/2	0	0.1086(15)	1
Sn(2)	6i	0.167(6)	0.334(12)	0	1

^a Not refined.

^b The crystal structure data have been deposited at Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany) under the deposition number CSD-431549.

phase.

To verify the guessed crystal structure for $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$, previously published XRD data [4] recorded at room temperature on a PIT wire previously heated to 480°C , and containing Bragg peaks attributed to the new phase were reanalysed by means of a multiphase Rietveld refinement (Fig. 6). For the refinement an input file for a $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ phase with NiMg_2 -structure was prepared having the lattice parameters from EBSD analysis, the fractional coordinates reported for $\text{NiCr}_5\text{Sn}_{12}$ [30]; and with Cu equally substituting 1/4th of the Nb atoms on the two Ni/Cr sites (see Table 2). Additionally, the confirmed phases (cf. Table 1) Cu_6Sn_5 , Cu and Nb (with 4 at% of Ta) were included whereas only traces of NbSn_2 and Cu_3Sn could be detected.

The lattice parameters for the $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ phase were adjusted by visual inspection of the observed and calculated diffraction pattern. The refined parameters for the $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ phase are summarised in Table 2. The mass fractions of the individual phases in the wire at room temperature after $T_{\text{max}} = 480^\circ\text{C}$

Fig. 6. Results of Rietveld refinement on the basis of synchrotron XRD data recorded from a PIT wire at room temperature after heat treatment up to 480°C : observed data points, calculated and difference curve (observed – calculated). A detailed visualisation of the Bragg peaks from the intermetallic compounds in logarithmic scale is displayed in the inset. Cu and Nb(Ta) peaks originate from the matrix material, whereas the intermetallic phases stem from the core and the reaction layer in between, raw data from Ref. [4].

Fig. 7. Reanalysis of the EBSD Kikuchi patterns from Fig. 4 with the suggested solution from Table 2: a) characteristic Kikuchi pattern of the hexagonal ($P6_22$) ternary intermetallic $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ and the proposed solution (mean angular deviation $\text{MAD} = 0.6^\circ$), b) phase map including $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ grains plotted in green (colour code compare Fig. 4a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

heat treatment were determined to be 62% Cu (Cu stabiliser), 26% Nb (unreacted tubes), 6% $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$, 3% Cu_6Sn_5 , 2% Cu_3Sn and 1% NbSn_2 . The fractional coordinates of the Sn atoms were refined, but did not change significantly from the starting values. Test refinements of the occupancies of Nb and Cu did improve the fit only slightly, but no apparent change in the description of the diffraction pattern could be recognised. The test refinements, moreover, did not significantly support preferred incorporation of the Cu atoms into either of the $M(1)$ and $M(2)$ sites. So the initial assumption that every fourth Nb atom was randomly substituted by Cu was kept.

The structure model of $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ obtained from the Rietveld refinement was employed to reanalyse the non-indexed patterns of the EBSD measurement from Fig. 4. In Fig. 7a a characteristic pattern that was indexed as $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ is depicted, showing apparently no discrepancies. The area which was indexed belonging to the ternary $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ phase is highlighted in green in Fig. 7b additionally to the phases which were already known from Fig. 4. Consequently the ternary phase not only forms at the reaction interface with the unreacted tube but also inside the powder core. This appears rather straightforward, as the diffraction peaks of $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ would not be visible in the diffraction pattern shown in Fig. 6, as the volume fraction would be in the order of the Cu_3Sn phase (also not seen in Fig. 6).

4. Discussion

Häussermann et al. [29] demonstrated that the crystal structure of many different binary transition metal stannide phases MSn_2 and $\text{M}_{1-x}\text{M}'_x\text{Sn}_2$ can be related with the valence electron concentration (VEC) and, therefore, with the composition of the corresponding intermetallic phase. In particular the sequence of CuMg_2 ($Fddd$) $\rightarrow$ NiMg_2 ($P6_222$) $\rightarrow$ CuAl_2 ($I4/mcm$) $\rightarrow$ CoGe_2 ($Aba20$) type structures was encountered upon increasing the VEC [23,29,30]. Thereby, the three structure changes occur at 13.9, 14.7 and 17.6 electrons per formula unit ($e^-/\text{f.u.}$). NbSn_2 exhibits a VEC of 13 and crystallises, in agreement with that sequence, in the CuMg_2 type [31]. Moreover, the above-mentioned distannides of NiMg_2 type occur in the range of 13.9–14.7 $e^-/\text{f.u.}$, except for MoSn_2 with 13.5 $e^-/\text{f.u.}$ Since the *in-situ* synchrotron data [4] indicate that the Bragg peaks of both NbSn_2 and Cu_6Sn_5 are significantly reduced in intensity prior to formation of the ternary phase at around 380 °C, it can be assumed that Cu partially replaces Nb in NbSn_2 . Thereby, like in other ternary $\text{M}_{1-x}\text{M}'_x\text{Sn}_2$ systems, the VEC is changed and a structure change can be induced. Adopting the chemical composition of 66 at.% Sn,

25 at.% Nb, 8 at.% Cu measured by TEM/EDX in the ternary phase by Cantoni et al. [9]; the VEC increases from 13 to 14.5 $e^-/\text{f.u.}$ upon the composition change from NbSn_2 to about $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$, surpassing the $\text{CuMg}_2 \rightarrow \text{NiMg}_2$ boundary of 13.9 $e^-/\text{f.u.}$ Adopting the VEC range ($13.9 \leq \text{VEC} \leq 14.7$) for the stability of the NiMg_2 type according to Häussermann et al. [29] the NiMg_2 type structure of $\text{Nb}_{1-x}\text{Cu}_x\text{Sn}_2$ may exist for $0.15 \leq x \leq 0.28$. In the current study 4 at.% Ta was contained in the Nb tube in solid solution, so it may be incorporated in the new phase if formed at least partially from the tube. However, no traces of Ta were found in the TEM/EDX measurements. Moreover, the phase was found also in wires containing only Cu, Nb and Sn, without any Ta traces [11]. Hence, this phase is expected to exist as a purely ternary Cu-Nb-Sn phase. Chemical similarity of Ta and Nb implies that the former can substitute the latter in $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$. In any case, the present results do not allow conclusion on whether $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ is a stable or only a metastable phase of the Cu-Nb-Sn system.

A similar but apparently binary phase was reported by Vandenberg et al. [33] to form between 230 and 380 °C during annealing of Nb/Sn multilayers, observed at the interface between molten Sn and solid Nb. This was supposed to be a metastable polymorph of NbSn_2 . The authors stated the crystal structure derived from Guinier film data to be a NiMg_2 -type C36 Laves phase. The C36-Laves phase structure, however, corresponds to the MgNi_2 structure ($P6_3/mmc$) [32] and not to the Mg_2Ni structure (space group $P6_222$, Strukturbericht notation C_4). In fact, the figure shown by Vandenberg et al. [33] corresponds to the Mg_2Ni type structure and not to a Laves phase. Moreover, the lattice parameters of $a = 5.68 \text{ \AA}$ and $c = 14.64 \text{ \AA}$ closely resemble those to found here for the $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ (see Table 2) and are untypical for a C36 Laves phase.

5. Conclusions

The crystal structure of a phase with the approximate formula $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$ occurring as intermediate phase during production of Nb_3Sn superconductor wires has been resolved on the basis of analysis of electron backscatter diffraction (EBSD) patterns and has been confirmed by Rietveld refinement on the basis of synchrotron powder-diffraction data. This phase is of the hexagonal NiMg_2 type structure with lattice parameters of $a = 5.645(1) \text{ \AA}$ and $c = 14.124(5) \text{ \AA}$. Following points can be concluded.

- (1) As the phase was prepared from Nb-4at.%Ta alloy tube containing a mixture of binary NbSn_2 and Sn powders as well as a Cu sheath, a small amount of Ta in that phase is not unlikely. A comparison with the literature and the chemical similarity between Nb and Ta suggests that this is a reasonable assumption. At the same time it is most likely that the phase can also exist in the absence of Ta. We cannot determine at this stage, however, whether this phase is a stable or a metastable phase in the ternary Cu-Nb-Sn or quaternary Cu-Nb-Ta-Sn systems.
- (2) The occurrence of the observed crystal structure type is compatible with a change of the valence electron concentration from 13 for NbSn_2 up to 14.5 $e^-/\text{f.u.}$ for $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$, provoking a structural transformation from CuMg_2 type to NiMg_2 type.
- (3) The phase evolution during Nb_3Sn wire processing influences the microstructure in the fully processed wire, and strong performance improvements of Nb_3Sn PIT wires are expected when a more homogeneous microstructure can be achieved [13]. Knowledge of the crystal structure of $(\text{Nb}_{0.75}\text{Cu}_{0.25})\text{Sn}_2$, which was unknown until now, is an important step towards a better understanding of the Cu-Nb-

Sn system. Nevertheless, experimental studies on the homogeneity range, multiphase equilibria and thermodynamic properties are necessary for predicting phase evolution and microstructure development during Nb₃Sn wire processing, and for optimising the wire architecture.

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References

- [1] B.T. Matthias, T.H. Geballe, S. Geller, E. Corenzwit, *Phys. Rev.* 95 (1954) 1435, <http://dx.doi.org/10.1103/PhysRev.95.1435>.
- [2] L. Bottura, G. de Rijk, L. Rossi, E. Todesco, *IEEE Trans. Appl. Supercond.* 22 (2012), <http://dx.doi.org/10.1109/TASC.2012.2186109>, 400 2008.
- [3] G. Ambrosio, *IEEE Trans. Appl. Supercond.* 25 (2015) 1, <http://dx.doi.org/10.1109/TASC.2014.2367024>.
- [4] M. Di Michiel, C. Scheuerlein, *Supercond. Sci. Tech.* 20 (2007) L55, <http://dx.doi.org/10.1088/0953-2048/20/10/L01>.
- [5] M.T. Naus, P.J. Lee, D.C. Larbalestier, *IEEE Trans. Appl. Supercond.* 11 (2001) 3569, <http://dx.doi.org/10.1109/77.919835>.
- [6] J.L.H. Lindenhovius, E.M. Hornsvelt, A. den Ouden, W.A.J. Wessel, H.H.J. ten Kate, *IEEE Trans. Appl. Supercond.* 10 (2000) 975, <http://dx.doi.org/10.1109/77.828394>.
- [7] S. Fürtauer, D. Li, D. Cupid, H. Flandorfer, *Intermetallics* 34 (2013) 142, <http://dx.doi.org/10.1016/j.intermet.2012.10.004>.
- [8] X. Wu, X. Peng, M.D. Sumption, M. Tomsic, E. Gregory, E.W. Collings, *AIP Conf. Proc.* 824 (2006) 504, <http://dx.doi.org/10.1063/1.2192388>.
- [9] M. Cantoni, C. Scheuerlein, P.-Y. Pflirer, F. de Borman, J. Rossen, G. Arnau, L.R. Oberli, P. Lee, *J. Phys. Conf. Ser.* 234 (2010) 022005, <http://dx.doi.org/10.1088/1742-6596/234/2/022005>.
- [10] C. Scheuerlein, M. Di Michiel, G.A. Izquierdo, F. Buta, *IEEE Trans. Appl. Supercond.* 18 (2008) 1754.
- [11] C. Scheuerlein, M. Di Michiel, G. Arnau, R. Flükiger, F. Buta, I. Pong, L. Oberli, L. Bottura, *IEEE Trans. Appl. Supercond.* 21 (2011) 2554, <http://dx.doi.org/10.1109/TASC.2010.2082476>.
- [12] C. Tarantini, C. Segal, Z.H. Sung, P.J. Lee, L. Oberli, A. Ballarino, L. Bottura, D.C. Larbalestier, *Supercond. Sci. Tech.* 28 (2015) 095001, <http://dx.doi.org/10.1088/0953-2048/28/9/095001>.
- [13] C. Segal, C. Tarantini, Z. Sung, P. Lee, B. Sailer, M. Thoenner, K. Schlenga, A. Ballarino, L. Bottura, B. Bordini, C. Scheuerlein, D. Larbalestier, *Supercond. Sci. Technol.* 29 (2016) 085003, <http://dx.doi.org/10.1088/0953-2048/29/8/085003>.
- [14] I. Pong, L. Oberli, L. Bottura, *Supercond. Sci. Tech.* 26 (2013) 105002, <http://dx.doi.org/10.1088/0953-2048/26/10/105002>.
- [15] C. Scheuerlein, M. Di Michiel, L. Thilly, F. Buta, X. Peng, E. Gregory, J.A. Parrell, I. Pong, B. Bordini, M. Cantoni, *J. Phys. Conf. Ser.* 234 (2010) 022032, <http://dx.doi.org/10.1088/1742-6596/234/2/022032>.
- [16] M.T. Naus, Ph.D. thesis, University Of Wisconsin – Madison, 2002. URL: http://fs.magnet.fsu.edu/~lee/asc/pdf_papers/theses/mtn02phd.pdf.
- [17] J.A. Parrell, Y. Zhang, M.B. Field, P. Cisek, S. Hong, *IEEE Trans. Appl. Supercond.* 13 (2003) 3470, <http://dx.doi.org/10.1109/TASC.2003.812360>.
- [18] M. Li, Z. Du, C. Guo, C. Li, *J. Alloy Compd.* 477 (2009) 104, <http://dx.doi.org/10.1016/j.jallcom.2008.09.141>.
- [19] L. Li, M. Han, *J. Appl. Cryst.* 48 (2015) 107, <http://dx.doi.org/10.1107/S1600576714025989>.
- [20] C. Scheuerlein, G. Arnau, P. Alknes, N. Jimenez, B. Bordini, A. Ballarino, M. Di Michiel, L. Thilly, T. Besara, T. Siegrist, *Supercond. Sci. Technol.* 27 (2014) 025013, <http://dx.doi.org/10.1088/0953-2048/27/2/025013>.
- [21] A. Gangulee, G.C. Das, M.B. Bever, *Metall. Trans.* 4 (1973) 2063, <http://dx.doi.org/10.1007/BF02643268>.
- [22] W. Burkhardt, K. Schubert, *Z. Metallkd* 50 (1959) 442.
- [23] T. Woelpl, W. Jeitschko, *J. Alloy Compd.* 210 (1994) 185, [http://dx.doi.org/10.1016/0925-8388\(94\)90136-8](http://dx.doi.org/10.1016/0925-8388(94)90136-8).
- [24] W.L. Bragg, *Philos. Mag.* 28 (1914) 255, <http://dx.doi.org/10.1080/14786440908635219>.
- [25] M.C. Neuburger, Z. Krist. 93 (1936) 158, <http://dx.doi.org/10.1002/zaac.19311970119>.
- [26] TOPAS V5.0. Bruker AXS, Karlsruhe, Germany, 2014.
- [27] Inorganic Crystal Structure Database on CD-ROM. Version 2016–1. FIZ Karlsruhe, Germany, and NIST, Gaithersburg, MD, USA.
- [28] A.V. Tkachuk, L.G. Akselrud, Y.V. Stadnyk, O.I. Bodak, *J. Alloys Compd.* 312 (2000) 284, [http://dx.doi.org/10.1016/S0925-8388\(00\)01116-6](http://dx.doi.org/10.1016/S0925-8388(00)01116-6).
- [29] U. Häussermann, S.I. Simak, I.A. Abrikosov, B. Johansson, S. Lidin, *J. Am. Chem. Soc.* 120 (1998) 10136, <http://dx.doi.org/10.1021/ja981347t>.
- [30] A.K. Larsson, S. Lidin, *J. Alloys Compd.* 221 (1995) 136, [http://dx.doi.org/10.1016/0925-8388\(94\)01412-4](http://dx.doi.org/10.1016/0925-8388(94)01412-4).
- [31] A.H. Gomes de Mesquita, C. Langereis, J.L. Leenhouts, *Philips Res. Rep.* 18 (1963) 377.
- [32] F. Stein, M. Palm, G. Sauthoff, *Intermetallics* 12 (2004) 713, <http://dx.doi.org/10.1016/j.intermet.2004.02.010>.
- [33] J.M. Vandenberg, M. Gurvitch, R.A. Hamm, M. Hong, *IEEE Trans. Magn.* 21 (1985) 819, <http://dx.doi.org/10.1109/TMAG.1985.1063612>.