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The crystal structure of $(Nb_{0.75}Cu_{0.25})Sn_2$ 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 $(Nb_{0.75}Cu_{0.25})Sn_2$. 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 $(Nb_{0.75}Cu_{0.25})Sn_2$. In the previous literature the $(Nb_{0.75}Cu_{0.25})Sn_2$ phase described here has occasionally been referred to as Nausite.

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 cooper 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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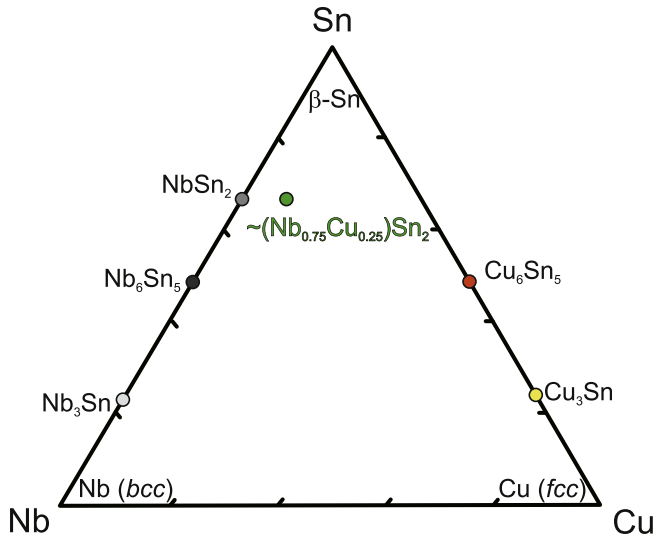

Fig. 1. Concentration triangle indicating the compositions of the various intermetallics encountered during the Nb_3Sn PIT wire processing including the ternary $(Nb_{0.75}Cu_{0.25})Sn_2$ phase analysed in the present work.

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 $NbSn_2$ 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 $NbSn_2$, Nb_6Sn_5 or Nb_3Sn [18].

In the present work a structure model for the $(Nb_{0.75}Cu_{0.25})Sn_2$ 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 $NiMg_2$ type structure (space group $P6_222$), 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.

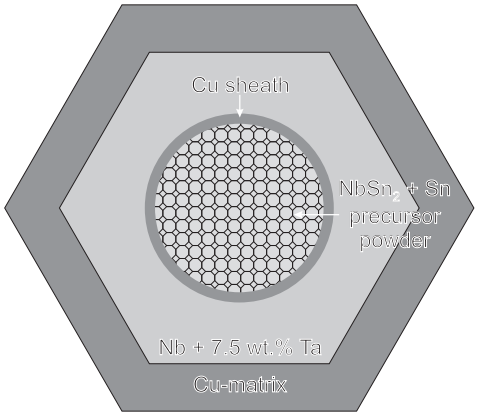

Fig. 2. Schematic structure of one individual filament of a Nb_3Sn composite wire before the heat treatment: $NbSn_2$ and Sn powder are enclosed by a hexagonal Nb(Ta) tube, which is lined inside with a Cu sheath; the surrounding Cu matrix interconnects the individual filaments within the wire.

2. Experimental

For the present study an Nb_3Sn 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 $NbSn_2$ + 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 $(Nb_{0.75}Cu_{0.25})Sn_2$ 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_6Sn_5	Cu_3Sn	$NbSn_2$	Cu	Nb
Reference	[21]	[22]	[23]	[24]	[25]
Space group	$P6_3/mmc$	$Pmmn$	$Fddd$	$Fm\bar{3}m$	$Im\bar{3}m$
a [Å]	4.192	5.49	9.874	3.61	3.2941
b [Å]		4.32	5.626		
c [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.