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Structure and electrical properties of $ScCu_4$ as bulk alloy and thin film

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Abstract

$ScCu_4$ is very sensitive to mechanical grinding. The influence of temperature and duration of recrystallization heat treatment on diffraction pattern and electrical conductivity of different specimens of $ScCu_4$ have been investigated. Cast alloys of $ScCu_4$, as well as ribbons obtained by rapid quenching of the melt, are crystalline. Thin films of $ScCu_4$ prepared by evaporation and by sputtering are amorphous. The latter materials are semiconductors while the former have electrical conductivities of the metal type.

Keywords: X-ray diffraction; Crystal structure; $ScCu_4$; Mechanical grinding; Recrystallization temperature

1. Introduction

Two variants of the phase diagram of the Sc–Cu binary system are known [1,2]. Three binary compounds occur in the system: ScCu, $ScCu_2$ and $ScCu_4$. According to the data of Markiv et al. [2] the $ScCu_4$ compound has a homogeneity range from 19 to 23 at.% Sc and crystallizes from the melt at 925°C. According to the phase diagram reported by Naumkin et al. [1] this compound melts at 925°C and has a constant composition. These authors established that $ScCu_2$ is formed peritectically at 890°C, while according to the data of Markiv et al. [2] it melts congruently at 990°C. In order to clarify the situation additional investigations would be necessary.

The crystal structure has been established for ScCu (CsCl structure type, space group $Pm\bar{3}m$, $a = 0.3256$ nm) [3] and $ScCu_2$ ($MoSi_2$ structure type; $I4/mmm$, $a = 0.3290$, $c = 0.8388$ nm) [4] compounds. The crystal structure of $ScCu_4$ is still unknown.

The compositions of binary Sc–Cu compounds are the same as found for the two other Ib elements Ag and Au: ScE, ScE_2 and ScE_4. All three ScE compounds occur in the CsCl structure type [3] and ScE_2 in the $MoSi_2$ structure type [4]. The compounds $ScAg_4$ and $ScAu_4$ belong to the $MoNi_4$ structure type, space group $I4/m$. The lattice parameters are $a = 0.6536$, $c = 0.40686$ nm for $ScAg_4$ [5] and $a = 0.6536$, $c = 0.4031$ nm for $ScAu_4$ [6]. So it seems possible that $ScCu_4$ is isotypic with $MoNi_4$ too. To verify this suggestion we decided to perform a complete crystal structure investigation of $ScCu_4$. During the X-ray diffraction (XRD) investigation of powdered specimens of $ScCu_4$ we noticed that $ScCu_4$ was very sensitive to grinding. In order to suppress the mechanical strains in the specimens we heated the powder at different temperatures. However, the conditions for a recrystallization heat treatment (temperature and duration) applicable to other alloys were not sufficient in the case of the $ScCu_4$ specimens. The reason for this phenomenon was also investigated during the crystal structure investigation of $ScCu_4$.

We investigated the preparation conditions of different specimens of $ScCu_4$ and the influence of these conditions on their XRD and electrical properties.

2. Experimental

The alloys were synthesized in an electric-arc furnace in an argon atmosphere by melting pieces of the components of the following purity Sc 99.92 wt.%, Cu 99.99 wt.%. Homogenization of the cast alloys was performed in evacuated quartz tubes at 400°C for

1000 h. X-ray structure investigations were made with the help of an automatic powder diffractometer DRON-4-07 (Cu Kα radiation, scanning with steps of 0.02° and 0.05°, the scanning time per point being 10 s).

Powder of $ScCu_4$ was hand ground in an agate mortar, pressed into nickel containers which were placed in evacuated quartz tubes and heated step by step at 400, 600, 800, 950 and 1000°C for 500 h.

Ribbons of $ScCu_4$ were obtained by rapid quenching of the melt $ScCu_4$ by ejection on to a rotating massive copper disk. The temperature gradient was 10^6 K s^{-1}.

Thin films of $ScCu_4$ were obtained on glass and ceramic substrates at room temperature or at temperatures up to 500 K. Some samples were prepared by thermal evaporation in vacuum (10^{-5} Pa) of pulverized powder of $ScCu_4$. The thin film samples were also deposited on semicrystallized glass substrates by magnetron sputtering of a target of $ScCu_4$ in an argon plasma (residual pressure of Ar in the system was 10^{-1} Pa).

A check of the chemical composition of the samples was made with the help of a microprobe analyser CAMEBAX, using five points for every sample. The accuracy of analysis was ±0.6%.

During preparation of the samples for electrophysical measurements the copper contacts on Cr sublayers were deposited by resistivity evaporation. The thickness of the thin-film samples was 1 μm, the thickness of the ribbons was 100 μm. The measurements of the electrical resistivity at 300 K and of the temperature dependency $\rho(T)$ of the samples in the temperature range 150–500 K were conducted in a vacuum cryostat using the four-point method.

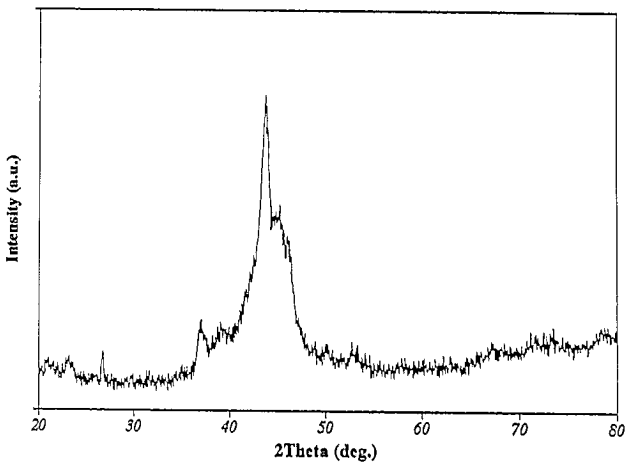

Fig. 1. XRD of cast $ScCu_4$.

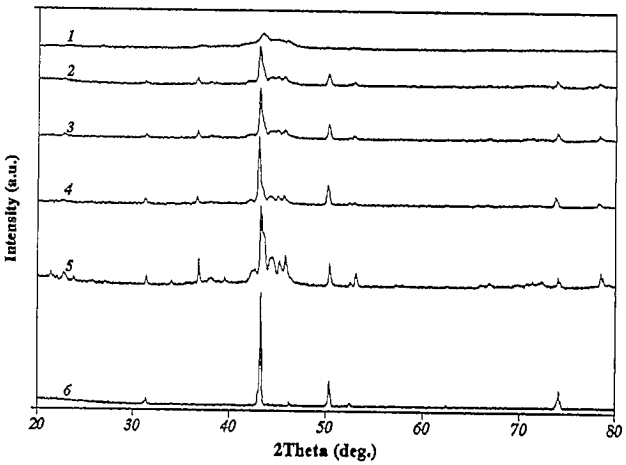

Fig. 2. XRDs of $ScCu_4$ previously homogenized at 400°C for 1000 h, powdered and recrystallized at different temperatures for 2 weeks: (1) without recrystallization (same specimen as in Fig. 1); (2) 400°C; (3) 600°C; (4) 800°C; (5) 950°C; (6) 1000°C.

3. Results and discussion

During the XRD investigation of $ScCu_4$ we noticed several interesting peculiarities. In the X-ray powder diffractogram of the cast alloy one can observe several broad maxima (Fig. 1). They are indicative of the large lattice strains which appeared during hand grinding for 0.5 h of the alloy pieces in the agate mortar. We tried to eliminate these strains by heating the powder for 2 weeks at 400, 600 and 800°C. After the heat treatment the powder was investigated without any extra mechanical operations. However, as can be seen from Fig. 2 (curves 2, 3, 4), the heat treatment at the temperatures indicated above was not sufficient. So we increased the temperature as much as possible, reaching the melting temperature of 925°C according to the data of Refs. [1,2]. The powder remained solid at even higher temperatures, i.e. at 950 and 1000°C. The XRD examination of the powders heated at 950°C and at 1000°C for 2 weeks gave indications of a possible high temperature phase transition in $ScCu_4$ (Fig. 2 curves 5, 6).

Our attempts to index automatically the diffractograms 5 and 6 in order to obtain the crystallographic data comprising symmetry and lattice parameters of $ScCu_4$ were unsuccessful. For this purpose we used a computer program described in Ref. [7]. However, even with the visible simplicity of diffractogram 6 compared with diffractogram 5, they could not be indexed.

We managed to extract from the cast alloy a piece of plate-like single crystal. Unfortunately it's quality was very poor. The only information obtained from Laue, rotation and Weissenberg methods of investigation of it was that it had tetragonal or pseudotetragonal symmetry, a body-centred Bravais lattice and a = 0.491, c = 0.698 nm. Having these data we could index only some of the reflections contained in the powder patterns 5 and 6. In the diffractograms, several reflec-

tions, including the strongest one, can be indexed as belonging to pure Cu, refined lattice parameter $a = 0.36190(4)$ nm. This result is in contradiction to the data of microscopic and microprobe analyses that indicated single phase composition of the sample (Table 1). Perhaps the unit cell structure of $ScCu_4$ contains fragments of the Cu structure in combination with other fragments.

For further investigations we need another single crystal of better quality. These investigations are now in progress.

The results of the investigation of the diffractograms reported above indicated a high inclination of $ScCu_4$ to structural distortions. Therefore we tried to investigate its inclination to amorphization and the influence of different factors on it.

It is well known that compounds crystallizing directly from the melt usually have no inclination to amorphization during rapid cooling of the melt (see for instance Ref. [8]). The ribbons of $ScCu_4$ obtained during rapid cooling of the $ScCu_4$ melt with a temperature gradient of 10^6 K s^{-1} were indeed crystalline (Fig. 3, curve 1), but the diffractogram changed sharply after mechanical hand grinding of the ribbon in an agate mortar for 0.5 h (Fig. 3, curve 2). During preparation of the ribbons we again observed melting of the alloy at temperatures higher than 1000°C, but not at 925°C. This is in agreement with the results obtained during heat treatment of powders of $ScCu_4$. So a re-examination of the Sc–Cu phase diagram in the range $ScCu_4$–$ScCu_2$ is necessary.

Methods of preparing amorphous alloys of congruently melting compounds by mechanical alloying of the components have been reported [8,9]. One of the necessary conditions of such alloying is as follows: the radius ratio of the atomic components should be close to 0.7 [9]. In the case of $ScCu_4$ this ratio is $r_{Cu}/r_{Sc} = 0.78$ ($r_{Cu} = 0.128$ nm, $r_{Sc} = 0.164$ nm). This indicates the possibility of preparing amorphous $ScCu_4$. Perhaps it would also be possible to mechanically amorphize the previously prepared $ScCu_4$ compound.

Extra hand grinding in an agate mortar for 0.25 h of the powder heated at 1000°C leads to broadening of diffraction peaks and lowering of their intensities (Fig. 4). For further distortion of the $ScCu_4$ lattice a high-energy mortar is necessary (which has not been available).

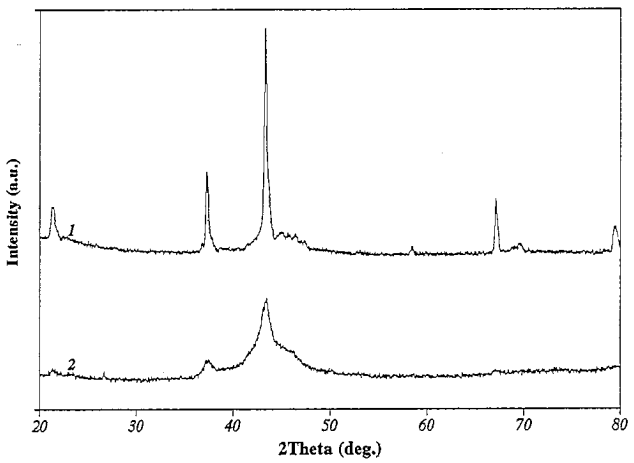

Fig. 3. XRD of $ScCu_4$ ribbon obtained by rapid cooling of liquid: (1) without grinding; (2) after grinding.

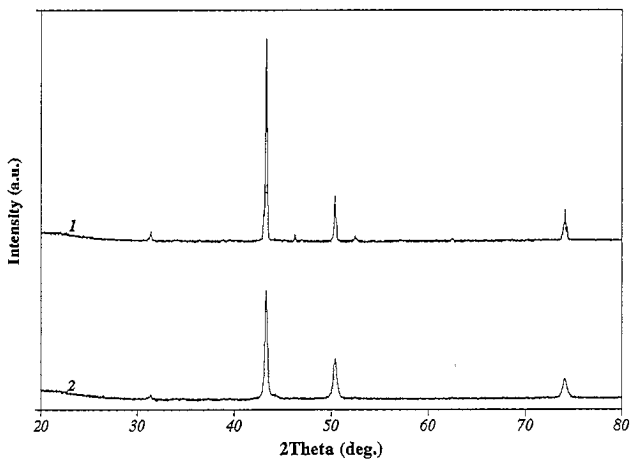

Fig. 4. XRD of $ScCu_4$: (1) fragment of curve 6 from Fig. 2; (2) after grinding.

Evaporation and sputtering from gaseous phase are two other methods for obtaining amorphous materials [8,10], but these methods are very sensitive to preparation conditions of the samples. Shifts in compositions of bulk and film specimens are possible.

A check of the sample compositions (with the help

Table 1
Data of microprobe analysis of samples of $ScCu_4$ obtained by different methods

N of point	Bulk		Film obtained by evaporation		Film obtained by sputtering	
	Sc (at.%)	Cu (at.%)	Sc (at.%)	Cu (at.%)	Sc (at.%)	Cu (at.%)
1	18.6	81.4	18.5	81.5	15.8	84.2
2	18.3	81.7	18.8	81.2	16.5	83.5
3	18.1	81.9	20.5	79.5	16.1	83.9
4	18.3	81.7	19.3	80.7	16.3	83.7
5	18.2	81.8	18.6	81.4	16.3	83.7

of microprobe CAMEBAX) indicated that the chemical composition of films agreed well with the composition of the bulk sample from which they were obtained (Table 1).

Diffractograms of the films obtained by thermal evaporation display one broad maximum in the low angle area at $s = 14.9\ nm^{-1}$ (Fig. 5, curve 1), which is typical of the amorphous state.

Films obtained by magnetron sputtering had an amorphous structure to, but the diffractograms of these samples differ from those obtained by evaporation. A shoulder of small intensity appears on the right-hand slope of the broad maximum, the centre of which occurs at $s = 24.6\ nm^{-1}$ (Fig. 5, curve 2).

Values of resistivity at $T = 300$ K for different samples are as follows: $\rho_{300\ K} = 10\ \mu\Omega$ cm for bulk $ScCu_4$; 100 ... 1000 $\mu\Omega$ cm ($T_S = 300$, 500 K) for films obtained by evaporation; $10^6 \ldots 10^5\ \mu\Omega$ cm for films obtained by sputtering; 1000 $\mu\Omega$ cm for ribbons.

The experimental temperature dependence of the conductivity, plotted as $\log\sigma = f(10^3/T)$ for different $ScCu_4$ samples is shown at the Fig. 6. Bulk, thin films (obtained by evaporation) and ribbons of $ScCu_4$ (curves 1, 2, 3) at the investigated temperature ranges ($T = 150 \ldots 500$ K) are characterized by metallic conductivity with small values of the thermal coefficient of the resistance. The character of these dependences are just as in metallic glass-type materials [11], where the Ziman theoretical model description for the mechanism of electrical conduction is usually used [12,13]. The temperature dependences of the electrical conductivity of crystalline $ScCu_4$ ribbons and amorphous thin films are the same. They point to a similar mechanisms of dispersion of carriers in microcrystalline and amorphous $ScCu_4$.

For thin films of $ScCu_4$ obtained by sputtering, the dependences $\log\sigma = f(10^3/T)$ are just as for nonregular semiconductor structures. Curve 4 on Fig. 6 presents a $\log\sigma = f(10^3/T)$ plot for films obtained by sputtering at $T_S = 300$ K. This can be described by $\sigma = \sigma_0 \exp(\Delta E/kT)$, which agrees with a thermal activation mechanism of the conductivity. The thermal activation energy, calculated from the $\log\sigma = f(10^3/T)$ plot is equal to 0.24 eV. At $T < 250$ K this dependence transforms to $\sigma = \sigma_0 \exp(B/T^n)$, where $n = 1/3 \ldots 1/4$ according to Ref. [14]. Transformation of this part of the $\log\sigma = f(10^3/T)$ plot for $T < 250$ K in Mott's model points to a mechanism of hopping of carriers near the Fermi level.

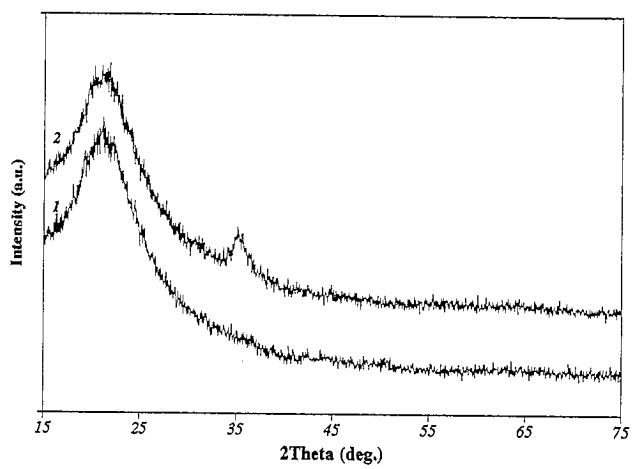

Fig. 5. XRDs of thin films of $ScCu_4$ obtained by (1) thermal evaporation and (2) magnetron sputtering.

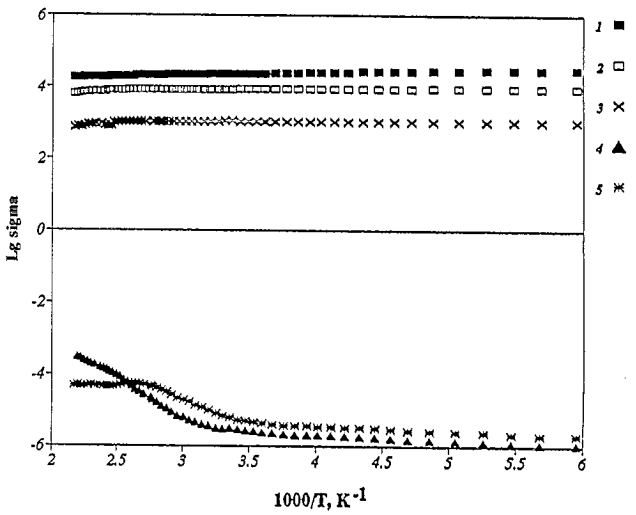

Fig. 6. $\log\sigma$ vs. $10^3 \times T^{-1}$ dependence of $ScCu_4$ specimens obtained by different methods: (1) bulk sample; (2) film obtained by evaporation; (3) ribbon; (4,5) film obtained by sputtering.

Curve 5 (Fig. 6) gives the $\log\sigma = f(10^3/T)$ dependence for films obtained by sputtering at $T_S = 500$ K. For $T < 250$ K the electrical conductivity changes to the carriers hopping mechanism. In the temperature region $250 < T < 350$ K there is activation of carriers occurring in widespread states. For $T > 350$ K a transition to the metallic type of conductivity appears. The complex character of the electrical conductivity in such materials can be explained by structural peculiarities of the deposits. The results of XRD investigations show the tendency to microscale inhomogeneities in these samples. This tendency is connected with the influence of noncontrollable admixtures of various types of growth mechanisms in the films, including oxide impurities.

4. Conclusions

$ScCu_4$ is very sensitive to mechanical strains, originating even from mechanical hand grinding. Structural homogenization by heat treatment for 2 weeks is possible only for temperatures, close to the melting temperature of $ScCu_4$, which is about 100°C higher than reported in the literature. Re-examination of the

Sc–Cu phase diagram at least in the range $ScCu_4$–$ScCu_2$ is necessary.

Thin films of $ScCu_4$ obtained by evaporation and sputtering are amorphous, but ribbons obtained by rapid quenching of the melt are crystalline and also sensitive to mechanical hand grinding.

Thin films of $ScCu_4$ obtained by sputtering have a semiconductor type of electrical conductivity. Bulk samples of $ScCu_4$, ribbons obtained by rapid quenching of the melt, and thin films obtained by evaporation are characterized by a metallic type of electrical conductivity.

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