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THE INFLUENCE OF TEMPERATURE ON THE CRYSTAL STRUCTURE OF $AuSn_4$

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Summary

The influence of the annealing temperature on the crystal structure of $AuSn_4$ was examined. X-ray studies of the $AuSn_4$ crystal structure were performed on powder samples as well as on single crystals. An order–disorder (O–D) transformation in $AuSn_4$ is claimed. The O–D transformation is connected with the existence of stacking faults along the [001] crystallographic direction. Despite these faults the volume of the unit cell remains essentially the same. Moreover, in the O–D state, long-range correlations may also exist. In the $AuSn_4$ crystals examined a superstructure which consists of six unit cells (as previously determined for fully ordered $AuSn_4$) was found.

1. Introduction

There are three stoichiometric and superconducting compounds known in the Au–Sn phase system: AuSn; $AuSn_2$; $AuSn_4$. A wide search in the literature on research into the Au–Sn phase system, comprising 81 items up to 1970, is collected in ref. 1. The basic crystallographic data and those concerning the temperature T_c of the transition to the superconducting state of the above compounds are collected in Table 1; the temperatures T_c show a considerable scatter. Undoubtedly, these differences result mainly from the different thermal histories of the samples examined in particular investigations. The Au–Sn alloys, in addition to the superconductive properties, show the appropriate strength for use in microelectronics and because of this there is great interest in these alloys. The influence of aging processes on the structure and properties of the Au–Sn alloys has been examined [11, 12]. An X-ray investigation of the influence of temperature on the crystal structure of the compounds AuSn, $AuSn_2$ and $AuSn_4$ has been undertaken at our Institute. The results of the investigations on $AuSn_4$ obtained to date are presented in this paper. Further investigations also including AuSn and $AuSn_2$ are continuing.

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TABLE 1

Data on the Au–Sn phase system

Phase	*Type*	*Space group*	*Cell parameters* (Å)	T_c (K)
AuSn	NiAs	$P6_3mc$	$a = 4.3222$, $c = 5.2222$ [2]	3.7 [3], 1.25 [4], 2.7[a] [5]
$AuSn_2$	TiO_2 (brookite)	*Pbca*	$a = 6.909$, $b = 7.037$, $c = 11.789$ [6, 7]	2.47 [8]
$AuSn_4$	$PtSn_4$	*Aba*2	$a = 6.446$, $b = 6.487$ [9]	2.38 [10], 5.1[a] [5]

[a] T_c for the amorphous sample.

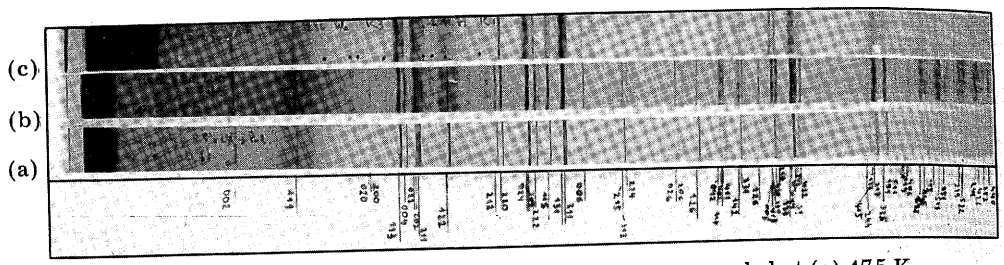


Fig. 1. Guinier photographs of the stoichiometric $AuSn_4$ alloy annealed at (a) 475 K, (b) 425 K and (c) room temperature.

2. Experimental details and results

The X-ray investigations on $AuSn_4$ were performed on powder samples as well as on single crystals. Spherical crystals of $AuSn_4$ were obtained according to the method described in refs. 13 and 14. The photographs of the powder samples were taken with a Guinier camera, and the photographs of the single crystals were taken with a Weissenberg goniometer camera, using Cu Kα radiation in both cases. The $AuSn_4$ alloy was quenched from the liquid state in water and then it was annealed for 3 days at 475 K. After annealing, the alloy was ground to powder in a mortar and divided into three parts. Two of the fractions were annealed again for 3 days, one at 475 K, the other at 425 K. The third part was left at room temperature. Guinier photographs of the samples prepared in this way were taken and are shown in Fig. 1. The sample annealed at 475 K gave sharp Bragg lines which are in good agreement with the model of the crystal structure given by Schubert and Roesler [9] (Fig. 1(a)). The corresponding lines on the photograph obtained from the sample annealed at 425 K are broadened and in addition the lines which satisfy the dependences $h + k = 2n$, $k + l = 2n$ and $l + h = 2n$ are relatively strong, whereas the remaining lines are weak; distinct side bands are clearly seen near some of them (Fig. 1(b)). On the photograph

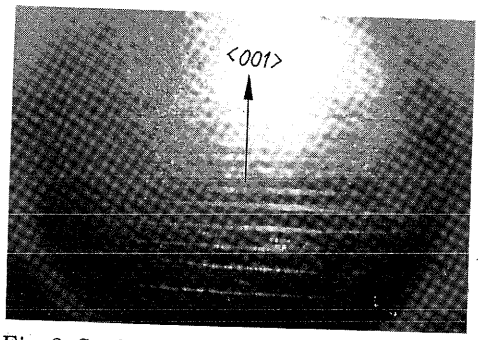
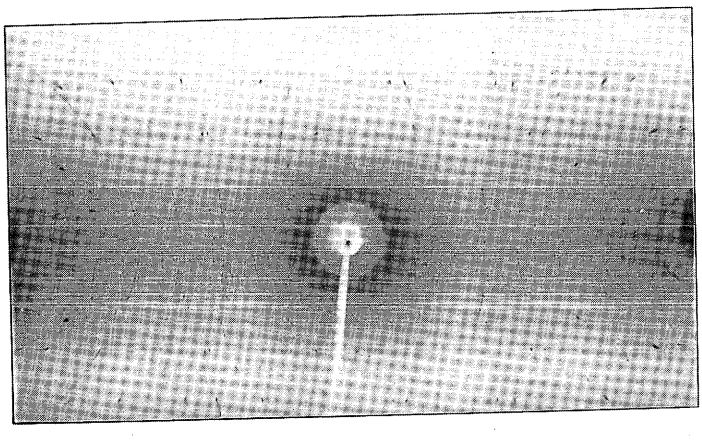


Fig. 2. Surface morphology of an $AuSn_4$ sphere 3 mm in diameter grown by the method described in refs. 13 and 14.

obtained from the sample which had been left at room temperature, the diffraction lines are even broader; the lines which satisfy the relations $h + k = 2n$, $k + l = 2n$ and $l + h = 2n$ are not present on the photograph and the splitting of pairs of lines hk, l vanishes. Moreover, traces of the compound $AuSn_2$ and lines of β-Sn are seen on the photograph (Fig. 1(c)). Another photograph of the sample annealed at 475 K was taken with NaCl as an internal standard. The lattice parameters of $AuSn_4$ refined on the basis of this photograph are as follows: $a = 6.502(1)$ Å; $b = 6.543(1)$ Å; $c = 11.705(2)$ Å.

Further information about the crystal structure of $AuSn_4$ was obtained from the crystals produced by cooling droplets of the liquid $AuSn_4$ alloy from 590 K to room temperature at a rate of about 500 K h^{-1}. The surface morphology of an $AuSn_4$ sphere 3 mm in diameter is presented in Fig. 2. Very distinct laminar lines are seen on the surface of the sphere. This sphere was mounted on a goniometer head with the laminar lines on its surface perpendicular to the rotation axis and photographs were taken by the oscillating crystal method. It was found that the sphere is not monocrystalline but has a highly developed texture of the ⟨001⟩ type. Such a sphere splits very easily along the planes determined by the laminar lines (perpendicular to the texture) and perfectly smooth flat rollers a fraction of a millimetre thick can be obtained from it without difficulty.

A sphere of $AuSn_4$ of about 0.3 mm diameter was chosen for the next photographs using the oscillating crystal method. The laminar lines were also seen on this sphere under the optical microscope. The sphere was oriented on the goniometer head in the direction [001] and a series of photographs of the oscillating crystal was taken; one such photograph is presented in Fig. 3. On the basis of these photographs it was found that reflections for which $l = 0, \pm 1, \pm 2, \ldots$ form the main layer lines and satellite reflections lie between them on separate layer lines. In addition, reflections of the $hk0$ type do not have satellite reflections and obey the dependences $h = 2n$ and $k = 2n$. Also, reflections of the hkl type do not have satellite reflections if $h + k = 2n$, $k + l = 2n$ and $l + h = 2n$. In contrast, if the reflections of the hkl type obey only the condition $k + l = 2n$, then the main reflection is weak and the



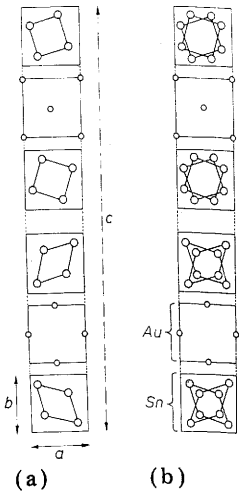


Fig. 3. An oscillation photograph of an $AuSn_4$ single crystal 0.3 mm in diameter (oscillation axis, [001]; oscillation range, 20°).

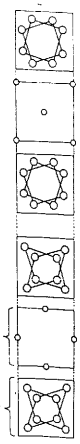
Fig. 4. The arrangement of gold and tin layers perpendicular to the [001] direction in $AuSn_4$ for (a) the ordered and (b) the O–D-type crystal structure. In (b) each tin layer occupies at random one of the two possible positions.

satellite reflections have Miller indices $hkl \pm \frac{1}{3}$. If $k + l = 2n + 1$, then the main reflection is missing and the satellite reflections have Miller indices $hkl \pm \frac{1}{6}$.

3. Discussion

The ordered crystalline structure of $AuSn_4$ consists of equal packs of layers shifted alternately and placed as shown in Fig. 4(a); two packs form an elementary cell. In each pack, two layers of tin atoms are placed antisymmetrically at both sides of the layer of gold atoms. These packs are mutually relatively weakly bound and it might be expected that their stacking would be disordered by high speed crystallization or because of mechanical deformation. The results confirm the existence of this kind of disorder in the samples of the $AuSn_4$ alloy examined; the structure of the alloy is highly dependent on the process of mechanical working as well as on the heat treatment.

It follows from the analysis of the Guinier photographs of the powder samples that after the mechanical grinding of an $AuSn_4$ alloy with the ordered crystal structure, the alloy appears to be in an order–disorder (O–D) state. Moreover, the elementary cell of $AuSn_4$ in the O–D state still consists of two packs but its symmetry is higher; an orthorhombic cell of the type A Bravais centring (the cell previously existing in the ordered structure) transforms into a tetragonal cell of the F type (preserving the same number



of formula units). It follows from this that most probably the mechanical grinding causes a slip of adjacent packs towards the same origin of the coordinate system in a statistical manner by vectors $\pm a/2 \pm b/2$ (Fig. 4(b)). The mechanical process of destruction of the ordering in the $AuSn_4$ structure probably results in a simultaneous partial decomposition of the phase $AuSn_4$ and the formation of the phases $AuSn_2$ and β-Sn (undoubtedly, mechanical deformation of the alloy is also a reason for the additional broadening of the diffraction lines (Fig. 1(a))). Such an alloy is not in a state of thermodynamic equilibrium and the annealing treatment causes an ordering of the alloy structure, as a result of which long-range correlations accompanied by the side-band effect appear (Fig. 1(b)) and the alloy eventually passes into the ordered state (Fig. 1(a)).

From the analysis of the photographs that were taken using the oscillating crystal method the long-range correlations within the crystals extend over six unit cells which apparently have tetragonal symmetry. The laminar lines observed on the surface of the $AuSn_4$ crystal probably result from the ordered distribution of defects and the presence of precipitates of the $AuSn_2$ and β-Sn phases. The following facts explain the existence of particularly advantageous conditions for the oriented configuration of the $AuSn_2$ and β-Sn precipitates with respect to the matrix $AuSn_4$ crystal.

(a) The crystal structures of both $AuSn_2$ and $AuSn_4$ have similar lattice parameters and consist of layers lying perpendicular to the c axis.

(b) For the $PtSn_4$ compound, which is isostructural with $AuSn_4$, it has been shown that crystals obtained from an alloy containing an excess of tin are surrounded by a thin layer of tin and the β-Sn layer is oriented in a definite way [9], *i.e.*

$$a_{PtSn_4} /\!/ a_{1Sn}$$

$$b_{PtSn_4} /\!/ c_{Sn}$$

$$c_{PtSn_4} /\!/ a_{2Sn}$$

(c) Faults in the stacking in the pack occur easily in the crystal structure of $AuSn_4$; this favours the formation of a laminar morphology of crystals and gives more freedom for movement of the phase boundaries of $AuSn_4$, $AuSn_2$ and β-Sn.

(d) Favier and Turpin [15] have observed perfect laminar ribbons of the compound $AuSn_4$ in a tin matrix with the composition of the alloy close to the eutectic composition (with a gold content in the alloy in the range 4 - 8 at.%), in spite of the fact that the isothermal conditions of growth postulated for such cases [16, 17] were not obeyed.

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