EFFECT OF COLD ECAE ON THE THERMOELECTRIC PROPERTIES OF Bi-Sb 15 At% ALLOY

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Abstract

A Bi-Sb 15 at% alloy was deformed at room temperature by Equal Channel Angular Extrusion (ECAE), in the attempt of reducing the grain size, hence the thermal conductivity.

SEM observations showed the presence of lamellar grains, with sub-micrometric thickness of lamellas.

The thermal conductivity substantially decreased by cold-work, however this positive effect on the figure of merit, Z, was more than counteracted by a huge increase of the electrical resistivity. In addition, the Seebeck coefficient decreased in absolute value at temperatures below 140 K. As a result, Z was severely depressed.

Annealing the cold-worked material at temperatures above 370 K produced a progressive recovery of the electrical conductivity and of the Z value. The original parameters were nearly restored by a thermal treatment at 393 K for 1 hour.

It is concluded that reduction of the grain size by the cold-work doesn't represent a viable route to increase Z in the Bi-Sb system.

1. Introduction

In a previous work [1] it was shown that the Bi-Sb 15 at% alloy can be homogenized by applying the Equal Channel Angular Extrusion (ECAE) process at 523 K to a Cu encapsulated as-cast alloy ingot. The homogeneity degree was seen to increase with the number of ECAE passes. After 8 passes, the figure of merit, Z, was higher than in single crystals, at temperatures above 150 K. Due to dynamic recrystallization during the ECAE process, the alloy presented, at the optical microscope observations, an average grain size of 20 μm.

To further improve Z, in this work we have tried to reduce the grain size, hence the thermal conductivity. To this goal, after homogenizing the Cu encapsulated as-cast alloy by ECAE at 523 K, we have performed 4 ECAE passes at room temperature.

2. Experimental

The ECAE process, first introduced by Segal [2], is sketched in Fig.1. When the sample crosses the channel intersection plane of trace OO', it undergoes a *simple* shear deformation, γ, given by [3]:

$$\gamma = 2 \cot (\phi/2 + \psi/2) + \psi \operatorname{cosec} (\phi/2 + \psi/2) \quad (1)$$

The *equivalent deformation*, ε, is given by [3]:

$$\varepsilon = 3^{-0.5} \gamma \quad (2)$$

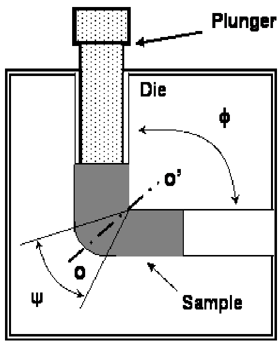

Fig. 1 Scheme of ECAE process.

Our experimental equipment was the same as described in paper [1]. The two channels, 40 mm in diameter, intersect at an angle $\Phi = 90°$; the entry channel is 120 mm in length, whereas the exit channel is 100 mm; the value of the Ψ angle is 40°, hence the true plastic strain after each pass is $\varepsilon = 0.98$. Six heating elements, 500 watt each, enable a uniform temperature in the channels and an accurate control of the extrusion temperature.

An alloy ingot, with a nominal composition $Bi_{0.85}$ $Sb_{0.15}$, was prepared in our laboratory, by melting and mixing the constituent elements, 5 N purity, in an evacuated quartz ampoule, at 773 K for 2 hours and water quenching from this temperature. The cast ingot was 15 mm in diameter and 60 mm in length. It was inserted in the middle of a Cu can, 40 mm in outer diameter and 110 mm in length, with the interposition of a 0.5 mm thick Nb tube as diffusion barrier. Finally, a Cu closure plug was applied.

The composite billet was firstly subjected to 8 ECAE passes at 523 K for alloy homogenization [1], then to 4 ECAE passes at room temperature, for cold-working the alloy. For all ECAE experiments, the so called *route C* was used, consisting into a 180° rotation of the billet around its long axis at each pass. Graphite was used as lubricant and the extrusion speed was about 10 mm/min. After extrusion, the Cu can and Nb barrier were mechanically removed.

Thermoelectric parameters, α, ρ, λ, were measured by a Quantum Design P.P.M.S. equipment, in the temperature range of 50 (or 80) to 300 K, on samples 15 mm long, with a cross section 2 x 3 mm^2.

Microstructure observations were made on fracture surfaces by a LEO 1430 SEM.

X-ray diffraction patterns were taken by a PANalytical mod. X Pert PRO equipment, using Cu K_α radiation.

3. Results and discussion

3.1 Effect of deformation at 300 K

Fig.2 shows the microstructure of the alloy after ECAE at room temperature, as revealed by SEM. A lamellar grain morphology is present, with thickness of lamellas ranging from 0.1 to 1 μm.

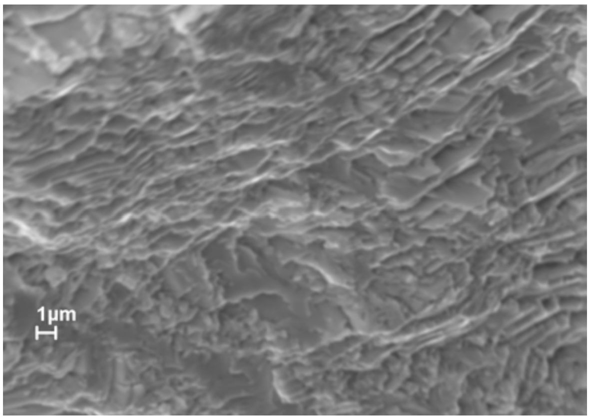

Fig.2 Microstructure of cold-worked alloy.

X-ray diffraction pattern of the cold-worked alloy was taken on different sections of the sample; no significant deformation texture was observed.

As an example, Fig.3 shows the results obtained on a section at 45° to the extrusion direction. By comparison with the X-ray pattern JCPDS 01-085-1331 of pure Bi, one realizes that all diffraction peaks are present; in particular, {00*l*} peaks are scarcely enhanced, in contrast to the expectation.

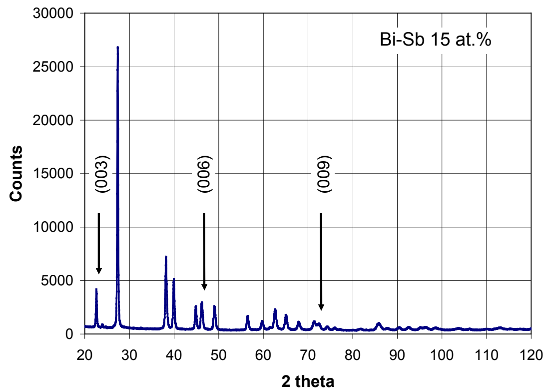

Fig.3 X-ray diffraction pattern after cold-work (45° to the extrusion direction).

The thermal conductivity of the cold-worked alloy is reported in Fig.4 (curve CW), together with the curve of the starting homogenized alloy (curve ECAE 523K) and other two curves to be discussed below.

It can be seen that cold-work substantially reduces the value of λ with respect to the fully homogenized state; the decrease reaches a maximum of 40% at 160 K.

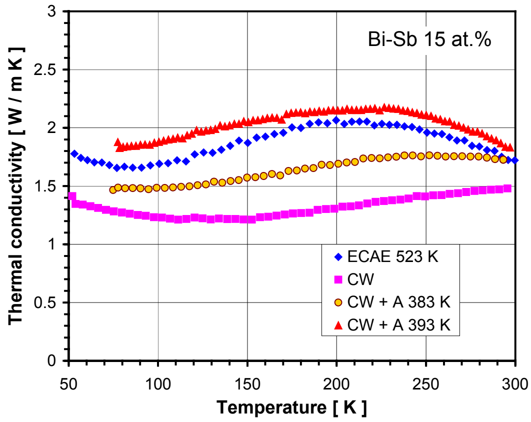

Fig.4 Thermal conductivity of the alloy in different structural states.

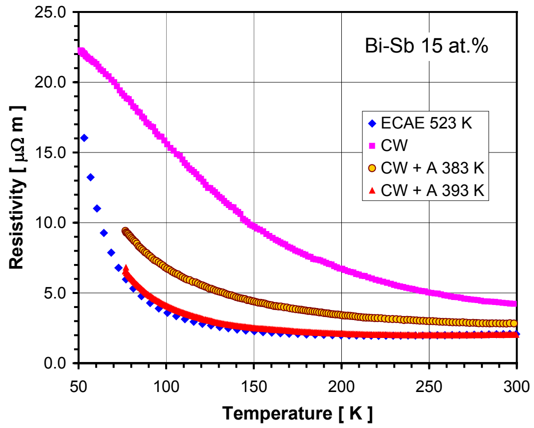

Fig.5 Electrical resistivity of the alloy in different structural states.

Fig.5 (curve CW) shows the electrical resistivity vs. temperature of the deformed alloy.

The effect of cold-work is dramatic: with respect to the homogenized alloy, the resistivity increases a factor of 2 at 300 K and reaches a factor of 4 at 100 K!

Concerning the Seebeck coefficient, the effect of cold-work is illustrated by the curve (CW) reported in Fig.6.

A slight improvement of α can be observed only in the range of 140 to 300 K; below140 K, α starts to decrease in absolute value with decreasing the temperature, in contrast to the behaviour of the homogenized alloy (curve ECAE 523K).

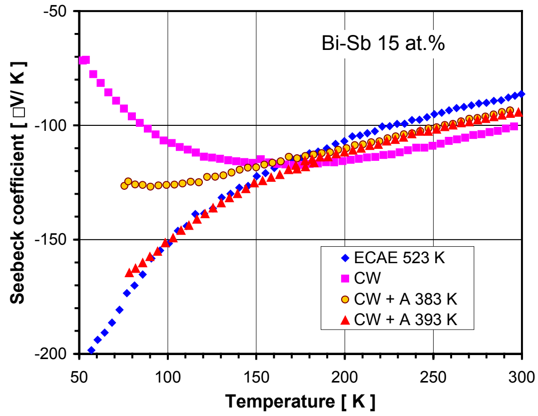

Fig.6 Seebeck coefficient of the alloy in different structural states.

As a result of the above values of the thermoelectric parameters, the figure of merit after cold work is severely worsened, as illustrated by the curve CW reported in Fig.7.

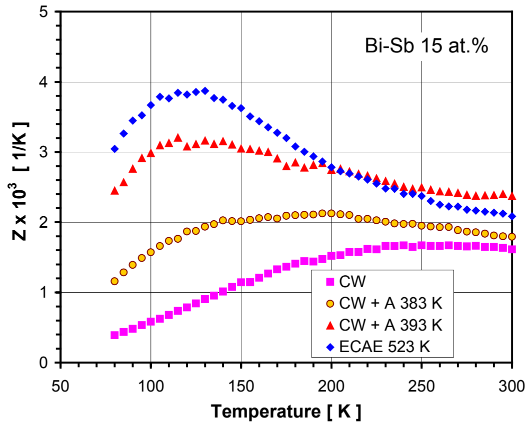

Fig.7 Figure of merit of the alloy in different structural states.

3.2 Annealing after cold-work

From the previous section it turns out that the electrical resistivity, ρ, is the main parameter that counteracts the positive effect of cold-work on λ and, as far as the temperature range of 140 to 300 K is concerned, also on α.

In order to decrease ρ, we have performed annealing experiments on the deformed alloy.

Fig.8 shows the resistivity values at 300 K after annealing 1 hour above 370 K.

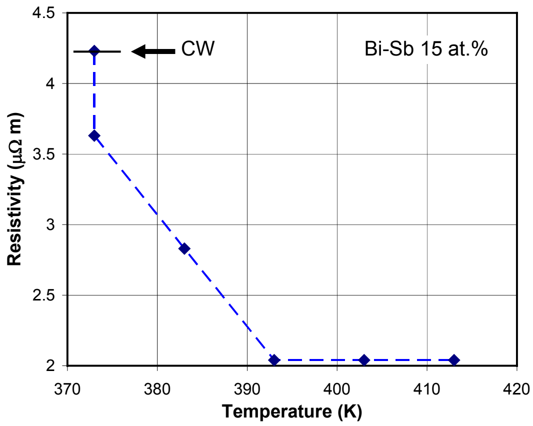

Fig.8 Resistivity values at 300 K after 1 hour annealing at increasing temperatures.

It can be noted that the value of the resistivity prior to cold-work can be recovered only after annealing at 393 K. This thermal treatment, however, causes also the restoration of all thermoelectric parameters, as evidenced by the curves (CW +A 393 K) reported in Figs. 4 to 6.

Annealing at intermediate temperatures, such as 383 K, is represented by the curve (CW + A 383 K) reported in the same figures. In any case, the value of Z is lower than the homogenized sample (see Fig.7).

The microstructure of the annealed samples, as observed at the optical microscope, is illustrated in Figs. 9 and 10, after annealing 1 hour at 383 K and 1 hour at 393 K, respectively.

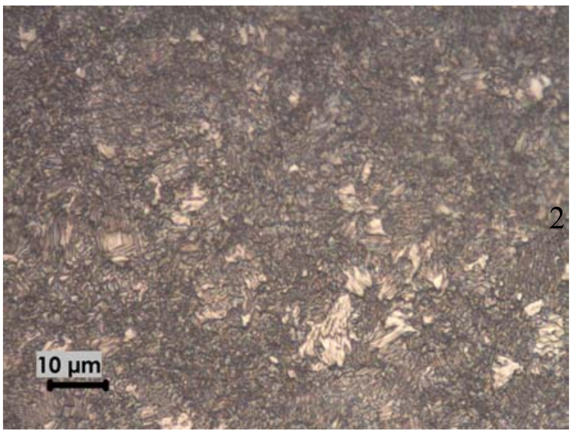

Fig 9 Optical micrograph of the CW alloy after annealing at 383 K.

Fig.10 Optical micrograph of the CW alloy after annealing at 393 K.

The average grain size is about 2 µm for the former sample and 20 µm for the latter.

Conclusions

The results of the present investigation indicate that it is impossible to increase the figure of merit of the Bi-Sb 15 at% alloy either by cold-work, or by annealing after cold-work.

It remains open the possibility of improving Z by performing ECAE in the temperature range of 350 to 400 K (warm ECAE); a promising alternative is also represented by the creation of a proper composite structure, with nanometer-scale Bi and/or Sb-rich inclusions.

References

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