Thermoelectric Properties of *In Situ* Formed $Bi_{0.85}Sb_{0.15}$/Bi-Rich Particles Composite

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A Bi-15 at.%Sb alloy, homogenized by equal channel angular extrusion (ECAE) at $T = 523$ K, has been treated just above its solidus temperature, causing segregation of a secondary Bi-rich phase at the grain boundaries. This process results in an *in situ* composite. The thermoelectric properties of the composite have been measured in the range of 5 K $< T < 300$ K. The results are compared with those of the homogeneous alloy. The presence of a Bi-rich phase improves the Seebeck coefficient at $T < 50$ K, and enhances the electrical conductivity by a factor of 1.4 at $T = 300$ K up to a factor of 3.4 at $T = 50$ K; unfortunately, the thermal conductivity also increases by about 50% in the same temperature range. As a result, the figure of merit, Z, is slightly suppressed above $T = 110$ K, but increases at lower temperatures, reaching a peak value of 4.2×10^{-3} K^{-1} at $T = 90$ K. The power factor considerably increases over the whole temperature range, rendering this material suitable as the *n*-type leg of a cryogenic thermoelectric generator for cold energy recovery in a liquefied natural gas plant.

Key words: Bi-Sb thermoelectric alloy, *in situ* composite, ECAE process, cryogenic thermoelectric generator

INTRODUCTION

Semiconducting single crystals of Bi-Sb alloys are recognized as the best *n*-type thermoelectric material operating at temperatures below $T = 200$ K.[1] The figure of merit of the Bi-15 at.%Sb alloy, measured along the trigonal axis, reaches the value of 6.5×10^{-3} at $T = 80$ K.[2]

Unfortunately, Bi-Sb single crystals are unreliable in practical devices, because of their intrinsic fragility. In fact, they present easy cleavage along planes normal to the trigonal axis. The best alternative for cryogenic applications is represented by polycrystalline Bi-Sb alloys.

In a previous paper[3] it was shown that homogeneous Bi-15 at.%Sb alloys can be easily obtained by processing the as-cast material by equal channel angular extrusion (ECAE) at $T = 523$ K. The homogeneity degree was seen to increase with the number of ECAE passes. After eight passes, the figure of merit was higher than in single crystals of the same composition, at temperatures above $T = 150$ K.

This result suggested[3] a potential application of this alloy as the *n*-type leg of a cryogenic thermoelectric generator operating at 130 K $< T < 290$ K for recovery of cold energy in a liquefied natural gas plant.

In this work, a dispersed second phase was introduced by *in situ* formation of a composite to improve the Z value for this alloy. According to the Bi-Sb phase diagram,[4] separation of a semimetallic Bi-rich phase occurs upon treating the homogenized alloy just above the solidus curve for this composition.

EXPERIMENTAL PROCEDURES

An alloy ingot with nominal composition of Bi-15 at.%Sb was prepared in our laboratory by melting and mixing the constituent elements (5 N purity) in an evacuated quartz ampoule at

$T = 773$ K for 2 h, with subsequent 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 a diffusion barrier. Finally, a Cu closure plug was applied.

The composite billet was firstly subjected to eight ECAE passes at $T = 523$ K for alloy homogenization,[3] using the so-called route C, consisting of a 180° rotation of the billet around its long axis at each pass. Graphite was used as a lubricant, and the extrusion speed was about 10 mm/min. After extrusion, the Cu can and the Nb barrier were mechanically removed.

Samples of 15 mm length, with a cross-section of 2 mm × 3 mm, were cut from the billet. The samples were treated for 2 min at $T = 567$ K, namely 1 K above the melting temperature of the alloy,[4] followed by water quenching, to promote separation of the Bi-rich phase.

Thermoelectric parameters, S, ρ, and k, were measured at Empa, Swiss federal laboratories of materials science and technology by using Quantum Design PPMS equipment, in the temperature range of 5 K $< T < 300$ K. The data concerning the homogeneous alloy were previously measured by the same equipment at CNR-LAMIA laboratory (Genova).

Microstructure observations were made on polished and etched (H_2O-25 vol.%HNO_3) sample surfaces by scanning electron microscopy (SEM, LEO 1430) with electron probe microanalysis (Oxford INCA x-sight 7353).

RESULTS AND DISCUSSION

Microstructure

Figure 1 shows an SEM image of the composite sample obtained by backscattered electrons. Grains have increased their average size from 20 μm, observed after the ECAE process,[3] to about 30 μm. In addition, most of them are surrounded by an area of brighter contrast, which has been identified by electron probe microanalysis as a Bi-enriched phase. It has long been reported that, in polycrystalline alloys, melting starts at grain boundaries (see, e.g., Ref. 5). It can thus be concluded that the brighter areas originate from this liquid Bi-rich phase present at $T = 567$ K and subsequent quenching from this temperature. Such a secondary phase, with a volume fraction of about 16% (determined using image analysis software), together with the residual alloy matrix, represent an *in situ* composite (ISC).

Figure 2 shows a sample zone containing a bright area as in Fig. 1, at higher magnification, with markers indicating sites 1–8 where alloy composition was determined by electron probe microanalysis. The values obtained (Table I) clearly show that the Sb content is higher than the original
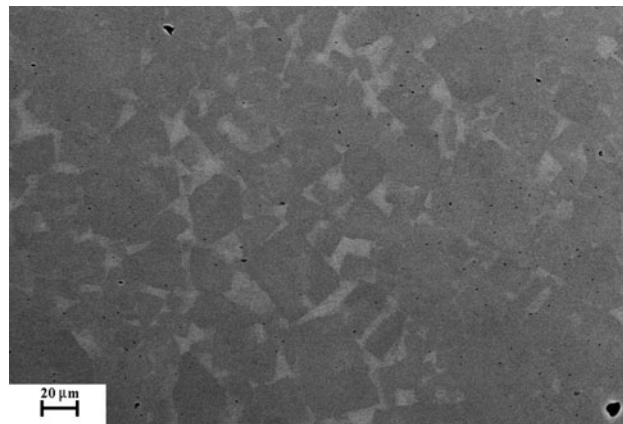

Fig. 1. Backscattered electron (BSE) SEM image of the ISC sample.

Fig. 2. BSE SEM image of an area of the ISC sample where the compositional analysis, reported in Table I, was performed.

Table I. Composition of the ISC sample at the points indicated in Fig. 2 determined by electron probe microanalysis

Position	Composition (at.%)	
	Bi	Sb
1	83.52	16.48
2	82.92	17.08
3	85.12	14.88
4	94.3	5.7
5	96.48	3.52
6	96.32	3.68
7	97.92	2.08
8	85.71	14.29

composition in the residual alloy matrix close to the grain boundary, whereas it drops to very low values inside the brighter area. At the center of the matrix grains (site 8), the composition remains unaffected, as one expects from both the short thermal treatment time and the low diffusion kinetics in the solid state.
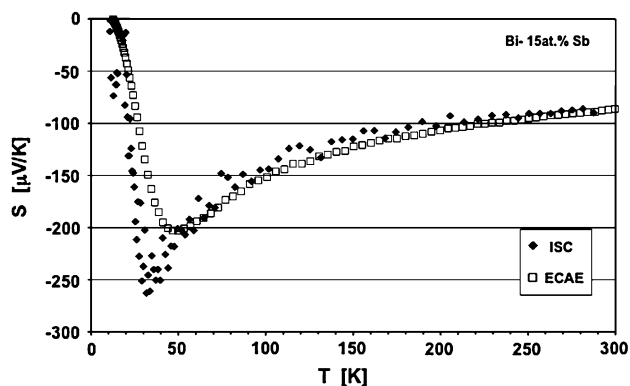
Fig. 3. Seebeck coefficient as a function of temperature. *Diamonds* refer to the ISC sample; *empty squares* refer to the ECAE-processed sample.
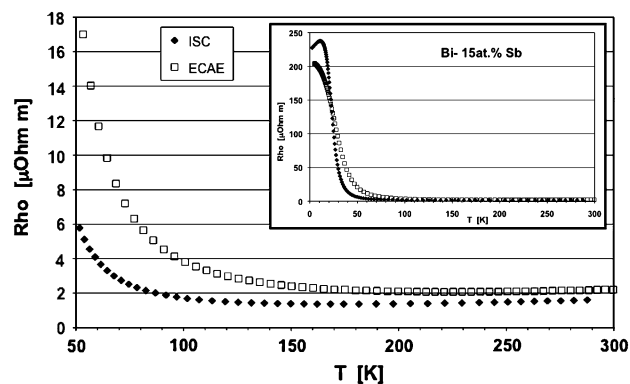

Fig. 4. Resistivity as a function of temperature from 50 K to 300 K. In the *inset* the data between 5 K and 300 K are plotted; at $T = 23$ K, a crossover between the resistivity of the two samples is visible.

Thermoelectric Properties

The variation of the Seebeck coefficient, S, of the ISC sample with temperature is reported in Fig. 3. In the same figure the curve of the homogenized alloy, named ECAE, refers to the sample of a previous study,[3] measured down to $T = 5$ K (unpublished results). It can be seen that the effect of the thermal treatment is to enhance S at temperatures below $T = 50$ K, shifting the peak position from $T = 50$ K to $T = 35$ K. This result appears surprising; considering the semimetallic character of the Bi-rich phase and its volume fraction (about 16%), a decrease of S should be observed. A possible explanation is to assume that the secondary phase is not connected in a continuous way throughout the sample. Under this hypothesis, the Seebeck coefficient of the composite is entirely ruled by the semiconducting residual alloy matrix. The increase of S can then be explained by the higher Sb concentration at the grain boundaries (Fig. 2, Table I). It has been reported in the literature[6] that the peak of the thermoelectric power for a Bi-16.5 at.%Sb single crystal (measured along a direction parallel to the trigonal axis) is both higher and shifted to lower temperatures with respect to a single crystal of composition Bi-14.4 at.%Sb. It appears reasonable to assume that a similar behavior may be valid for polycrystalline alloys as well.

The electrical resistivity, ρ, measured in the temperature range of 50 K $< T <$ 300 K, for both ISC and ECAE samples is reported in Fig. 4; in the inset, the data are extended down to $T = 5$ K. Both samples show the characteristic behavior of Bi-Sb alloys with an Sb atomic content between 7% and 22% throughout the temperature range.[6,7] It can be observed that the residual electrical resistivity values are one order of magnitude higher than those reported for single crystals.[6,7] According to the literature,[7] this indicates a very high degree of material purity. Comparing the two samples, the presence of Bi-rich areas around grain boundaries allows an alternative, less resistive pathway for the
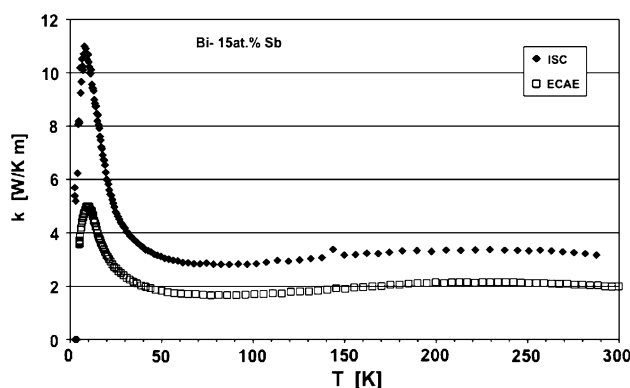
Fig. 5. Thermal conductivity as a function of temperature for ISC and ECAE samples.

charge carriers, reducing ρ by a factor of 1.4 at $T = 300$ K up to a factor of 3.4 at $T = 50$ K.

At low temperatures the resistivity behavior is strongly affected by the residual impurity concentration of the materials. Effects can be observed for concentrations below 10^{12} impurity atoms/cm^3. As a consequence, the different curves for the two samples (with nominal purity 10 ppm), including their crossover at $T = 23$ K, cannot be interpreted in detail.

Figure 5 shows the thermal conductivity, κ, of the alloy with the two different microstructures. Similar to previous studies,[3] the raw κ values have been corrected in the data analysis by removing the contribution from radiation losses, which become significant at $T > 80$ K. It can be seen that, for temperatures below $T = 20$ K, where κ is entirely dominated by the lattice contribution, the peak value of the ISC sample is a factor of 2.2 higher than that of the ECAE sample. This result can be explained by the semimetallic Bi-rich phase having a much higher phonon thermal conductivity than the semiconducting residual matrix.[8] In the temperature range of 20 K $< T <$ 300 K, when the electronic contribution to κ increases with increasing
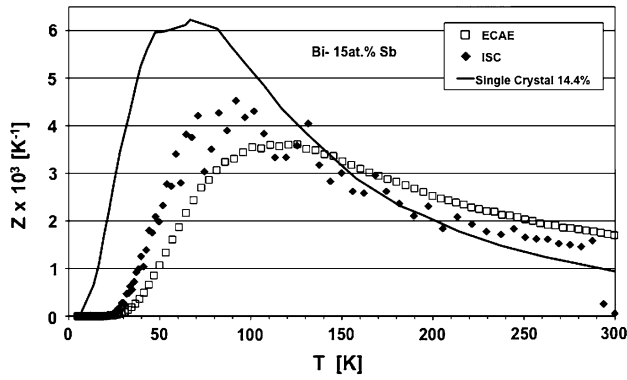
Fig. 6. Z values for the samples as a function of temperature. The *continuous curve* refers to the Bi-14.4 at.%Sb single crystal reported in Ref. 6.
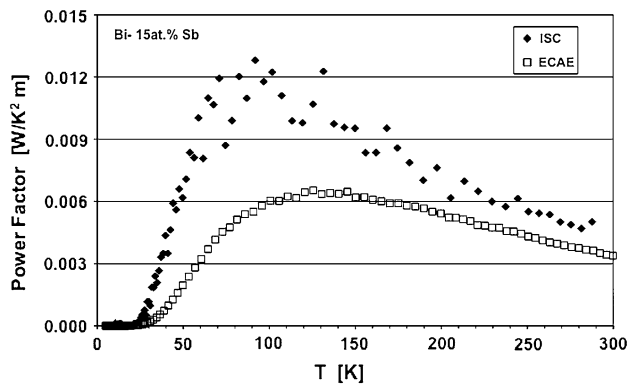

Fig. 7. Comparison between the power factors of ECAE and ISC samples for 10 K $< T <$ 300 K.

temperature, both thermal conductivity curves exhibit similar behavior, with the thermal conductivity of the ISC sample remaining about 50% higher than that of the ECAE sample.

From the measured values of the Seebeck coefficient, electrical resistivity, and thermal conductivity, the figure of merit $Z = S^2/\rho\kappa$ was calculated and is reported in Fig. 6. For comparison, the result for a single crystal of similar composition (Bi-14.4 at.%Sb) is also plotted.[6] At temperatures above $T = 160$ K, it is shown that the figure of merit of the ISC sample is comparable to that of the single crystal, whereas the ECAE sample shows the highest Z values above $T = 150$ K. At temperatures below $T = 110$ K, the figure of merit of the ISC sample exceeds the ECAE sample, reaching a maximum Z value of 4.2×10^{-3} K^{-1} at $T = 90$ K, which is among the highest ever reported for a

polycrystalline Bi-Sb alloy in this temperature range.

Figure 7 shows the power factor S^2/ρ of the alloy in both structural states. In this case, the behavior of the composite sample is always improved with respect to the homogeneous alloy, reaching a peak value of 1.25×10^{-2} W m^{-1} K^{-2} at $T = 90$ K. By comparison, the corresponding value calculated for the Bi-14.4 at.%Sb single crystal[6] is 1.30×10^{-2} W m^{-1} K^{-2}.

It is important to mention that, for the cryogenic thermoelectric generator application referred to in the "Introduction," the power factor is a very important parameter. In fact, for this application, the aim is to recover cold energy that would otherwise be wasted. Hence, the maximum obtainable output power, rather than the maximum conversion efficiency, is the target of choice.

CONCLUSIONS

A homogeneous Bi-15 at.%Sb alloy was treated for 2 min just above its melting temperature, causing segregation of a Bi-rich phase at the grain boundaries, thus forming local inhomogeneities, an *in situ* composite.

The figure of merit of the composite, with respect to the homogeneous alloy, is slightly suppressed above $T = 110$ K, but increases at lower temperatures, reaching a peak value of 4.2×10^{-3} K^{-1} at $T = 90$ K.

The power factor of the composite is significantly higher, which favors the application of this material as the *n*-type leg of a cryogenic thermoelectric generator, operating in the temperature range of 130 K $< T <$ 290 K, for recovery of cold energy of a liquefied natural gas plant.

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