TiNiSn: A Gateway to the (1,1,1) Intermetallic Compounds

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Abstract

Recent awareness of the transport properties of Skutterudite pnictides has stimulated an interest in numerous other intermetallic compounds having a gap in the density of states at the Fermi level including the MNiSn compounds where M=(Ti, Zr, Hf). These intermetallic 'half-Heusler' compounds are characterized by high Seebeck coefficients (-150 to -300 μV/deg.) and reasonable carrier mobilities (30 to 50 cm^2/V-s) at room temperature which make them attractive candidates for intermediate temperature thermoelectric applications. Samples of TiNiSn were prepared by arc melting and homogenized by heat treatment. The temperature dependence of the electrical resistivity, Seebeck coefficient, and thermal diffusivity of these samples was characterized between 22°C and 900°C. The electrical resistivity and thermopower both decrease with temperature although the resistivity decreases at a faster rate. Electrical power factors in excess of 25 μW/cm-°C^2 were observed in nearly single phase alloys within a 300 to 600°C temperature range. A brief survey of other selected ternary intermetallic compounds is also presented.

Introduction

The search for new thermoelectric materials is shifting from binary to ternary and higher order compounds. While at least one transport parameter is known about most (~ 85%) of the 4,000 experimentally known binary alloys, this figure drops to only ~5% of the 161,700 ternary alloys. In other words, there are some 153,000 compounds that are essentially unknown in terms of structure and properties. Several recent studies of the transport properties of an interesting class of ternary intermetallic compounds such as MNiSn (M = Ti, Zr, Hf) have shown that these compounds crystallize in the MgAgAs structure and are characterized by the existence of a gap or pseudo-gap in the density of states at the Fermi level [1,2,3,4]. This feature makes them attractive candidates for a survey of thermoelectric properties because the gap gives rise to semiconducting-like transport properties. The most intriguing property from a thermoelectric viewpoint is that of a large room temperature thermopower, on the order of -300 μV/°C. Of the three primary macroscopic quantities that affect a material's figure of merit (electrical conductivity, thermopower, and thermal conductivity), the thermopower is probably the most difficult to predict a priori and also to engineer. Therefore, a good starting point for a systematic search for high figure of merit materials are high metal content compounds having large thermopowers, as is the case for TiNiSn. While the dimensionless figure of merit of TiNiSn itself is unlikely to exceed that of conventional materials, a good understanding of the transport properties of this interesting compound is expected to provide insight into the feasibility of similar ternary compounds through substitutional alloying. Previous studies have investigated substitutions for the Group IVA transition metal [5] and for the Group VIIIA transition metal [6]. Other systematics remain unexplored. Little published data exists on the orthorhombic TiNiSi and TiNiGe compounds. Although strictly not Heusler alloys, these systems may provide useful information on the differences between intermetallic compounds with and without a gap. While alloy theory predicts limited solubility for Si or Ge in TiNiSn, the extent of solid solubility as a substitutional replacement for tin and the effect on the band structure and the thermoelectric properties remains unknown. Other ternary compounds are known to crystallize in the MgAgAs structure [7], such as

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the RPtSb where R= heavy lanthanide element and may be of interest as thermoelectric materials. Furthermore, it is hoped that the results of this research, coupled with that of other laboratories, will motivate subsequent investigations into the myriad of ternary intermetallic compounds having semiconducting-like transport properties.

Experimental Details

Stoichiometric quantities of Ti, Ni, and Sn were weighed out and arranged on a water-cooled copper hearth. Arc melting was accomplished by first melting the Ni and Sn together and then adding the Ti to form a smooth button. The button was turned over six times and remelted before arc-casting into a rod. The as-cast rod was sectioned for metallography and Hall coefficient measurements. The remainder of the rod was wrapped in Ta, sealed in quartz, and heat treated at 840°C for 3 weeks. Another set of samples was cut for metallography and Hall coefficient from the heat treated rod and a portion of the remainder was subjected to a final heat treatment of 950°C for a period of 2 weeks. No discoloration on the inner surface of the quartz was observed nor was there any noticable change in the ductility of the Ta wrapping. X-ray diffraction patterns of the samples were obtained with an automated powder diffractometer using Cu Kα radiation. Disk-shaped samples were characterized for their electrical properties at room temperature by a Hall effect measurement. Following Hall effect measurement, the disks were sectioned into rectangular parallelepiped-shaped bars and instrumented for electrical resistivity and Seebeck coefficient measurements from 22°C to 900°C. The measurement procedures are described in a previous publication [8].

Two samples were prepared at the University of Virginia by a similar arc casting procedure. These samples were subsequently heat treated at 800°C for various amounts of time as described in a previous publication [9]. In their paper, values of the room temperature Seebeck coefficient, electrical resistivity, and thermal conductivity were shown after annealing for up to 6 weeks. The temperature dependence of the electrical resistivity and Seebeck

coefficient of their samples after 1and 4 weeks at 800°C is presented and discussed later.

TiNiSi samples were also prepared for this survey by arc casting and heat treating. Dramatic differences between the cubic Sn and the orthorhombic Si compounds were observed.

Results and Discussion

I. Samples prepared at Ames Laboratory: Metallographic results showed the as-cast TiNiSn sample to be multiphase with clearly observed dendritic segregation, as shown in Fig. 1. The amount of segregation decreased upon application of a 3 week heat treatment at 840°C and a subsequent 2 week heat treatment at 950°C as shown in Figs. 2 and 3, respectively, albeit the material remained multiphased. The material was, however, clearly more homogeneous following the 950°C heat treatment, which gave rise to improved electrical properties as shown below.
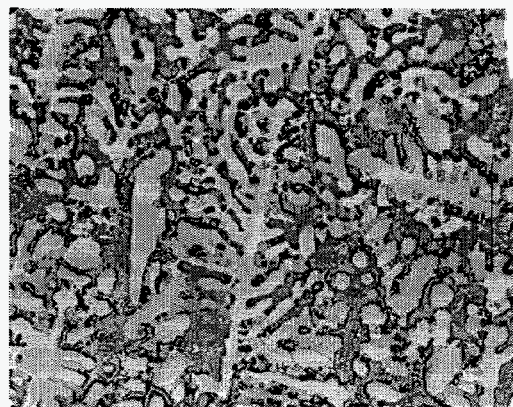

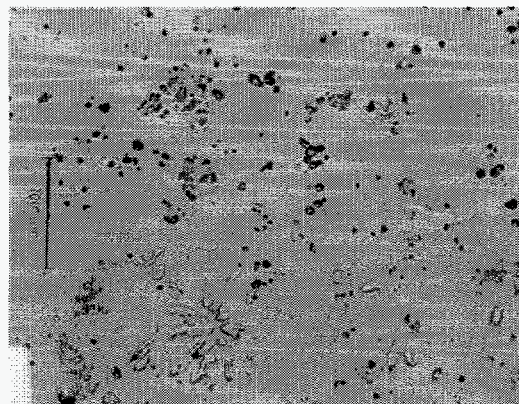Fig. 1. Microstructure of as-cast and electropolished TiNiSn (250X)

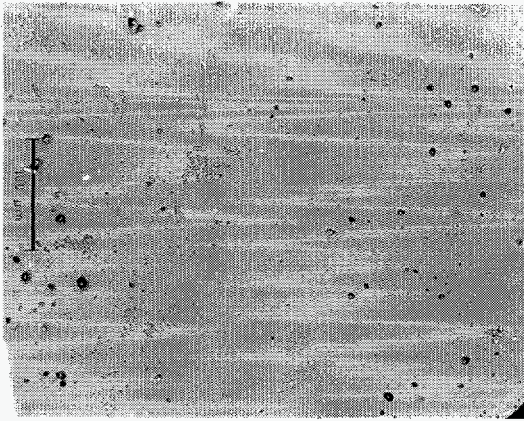Fig. 2. Microstructure of TiNiSn after 3 week heat treatment at 840°C (250X)

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Fig. 3. Microstructure of TiNiSn after 3 week heat treatment at 840°C (Fig. 2) followed by an additional 2 week heat treatment at 950°C (250X)

A small amount of material was removed from the 2 week at 950°C heat treatment sample and ground for evaluation by X-ray diffraction. The pattern is reproduced in Fig. 4.
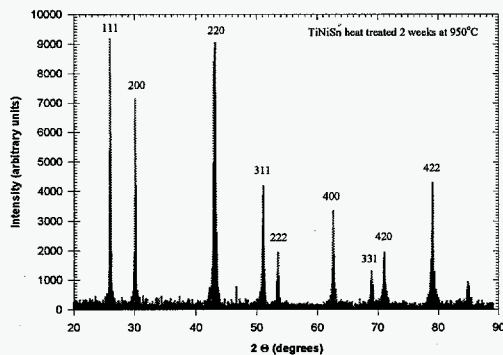

Fig. 4. X-ray Diffraction Pattern of TiNiSn Prepared by Arc Melting and Annealed for 2 Weeks at 950°C

All reflections can be indexed to a face centered cubic lattice and the amount of second phase is apparently less than five percent. The lattice parameter was determined to equal 0.5930 nm using a Nelson-Riley extrapolation routine, giving reasonable agreement with values reported by other researchers. In fact, the U. of Virginia group reported a lattice parameter of 0.5941 nm on their samples using different starting materials, a different heat treatment, and a different diffractometer. A summary of the room temperature electrical properties of some of these alloys is provided in Table I. The differences in the conduction mechanism between the semiconductor-like TiNiSn and semimetallic TiNiSi is obvious. From the slope of the intrinsic conductivity (see below) the

magnitude of the energy gap of TiNiSn is estimated from $\sigma = \sigma_o \exp(-Q/kT)$ to be on the order of 0.1 to 0.2 eV. However, the TiNiSi, crystallizing in an orthorhombic structure, shows no evidence of a gap.

Table I. Room Temperature Electrical Properties of TiNiX Alloys (X=Si or Sn)

Sample	ρ (mΩ-cm)	n (x10^{18}cm^{-3})	μ (cm^2/V-s)
TiNiSn IHT	14.8	8.0	53.0
TiNiSn IIHT	11.4	15.0	36.7
TiNiSi as cast	0.98	3140	2.0
TiNiSi HT	0.68	2670	3.4

note: IHT = 3 weeks at 840°C, IIHT = 2 weeks at 950°C
TiNiSi HT refers to 12 days at 1100°C

A usable thermoelectric material is generally expected to have a band gap of at least 5kT, which, at 300K has a value of 0.13eV. TiNiSn, which is intrinsic above room temperature, only marginally satisfies this requirement. Nonetheless, this material displays interesting electrical properties within the intrinsic conduction regime. The high temperature electrical resistivity, ρ, Seebeck coefficient, S, and power factor, S^2/ρ, of two TiNiSn alloys arc melted at Ames and subsequently annealed are shown in Fig. 4.
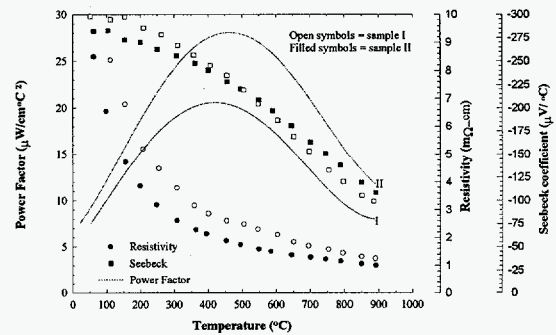

Figure 4. Electrical resistivity, Seebeck coefficient, and power factor of arc melted and annealed TiNiSn. Sample I = 3 week heat treatment at 840°C, Sample II = Sample I + additional 2 week heat treatment at 950°C.

Both samples display qualitatively similar electrical behavior although the resistivity of the material which had been heat treated at 950°C is lower than that of the corresponding sample heat treated at 840°C. This seems reasonable

considering that a more homogeneous microstructure will provide fewer second phase scattering sites. Clearly, control of microstructure will be a critical parameter in optimizing the thermoelectric properties of these alloys. The decrease in resistivity with temperature is consistent with that of an intrinsic semiconductor. The Seebeck coefficient of the two samples is similar and is sufficiently large to drive the power factor to a maximum of 27 μW/cm-deg.^{2} near 500°C in the material heat treated at 950°C for 2 weeks. Due to the higher resistivity, the power factor of the 840°C sample maximized at 21 μW/cm-deg.^{2}. Interestingly, the power factor increases with increasing temperature in the lower temperature range, even though the material should be operating in or quite near the intrinsic conductivity range. The magnitude of the power factor is comparable with that of state-of-the-art silicon-germanium alloys, although Si-Ge can be used at a much higher operating temperature than TiNiSn. Continuous cooling data was obtained after reaching the maximum temperature and no evidence of hysteresis was observed.

II. Samples prepared at the Univ. of Virginia:

Two rectangular parallelepiped-shaped samples of TiNiSn were cut from an arc melted and heat treated sample prepared at the University of Virginia. These samples were instrumented and characterized for high temperature electrical resistivity and Seebeck coefficient in the same manner as applied to the alloys prepared at Ames. The results of these measurements are shown in Fig. 5.
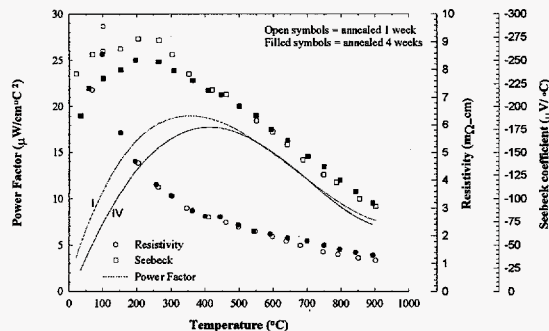

Figure 5. Electrical resistivity, Seebeck coefficient, and power factor of arc melted and 800°C annealed TiNiSn. Sample designation: I = 1 week heat treatment and IV = 4 week heat treatment.. (Samples were prepared at the University of Virginia)

The Seebeck coefficient of both samples increases slightly with temperature to about 300°C and decreases thereafter. This behavior is qualitatively different from the samples prepared at Ames in that the latter alloys show a continuously decreasing Seebeck coefficient with temperature throughout the entire temperature range. The electrical resistivity of both sets of samples show similar behavior. The power factor of the U. of Virginia samples increases to a maximum of near 20 μW/cm-deg.^{2} in the 300 to 400°C range. It is noted that the maximum power factor of the Ames' 840°C heat treated sample is similar to that of the U of Virginia alloys but that the application of the additional heat treatment at 950°C has improved the power factor. The exact cause for the improvement is not known at this time, however, some differences in processing are worth mentioning. The U. of Virginia group placed the samples in alumina crucibles which were in turn sealed within quartz ampoules. They subsequently observed formation of a metallic coating on the inner wall of the ampoule following the heat treatment. In contrast, the Ames group wrapped the samples in Ta before sealing in quartz and no coating on the ampoules was observed. Moreover, no noticeable change in the ductility of the Ta was observed, which would have suggested that a reaction between the sample and the wrapping occurred. Clearly, additional studies are needed to identify and control the heat treatment conditions required for the optimum power factor.

The thermal conductivity of various heat treated specimens have been measured at room temperature by the Virginia group and found to lie in the 40 to 60 mW/cm-deg. range. From the above data, the high temperature thermal transport in these alloys is expected to be dominated by an increasing electronic component which might offset any T^{-1} phonon scattering decrease. Taking the lower value for the thermal conductivity, a reasonable estimate for the optimized ZT of this material would be 0.45 to 0.50 within the 300°C to 600°C range.

III. Other (1,1,1) Compounds

A survey of the RPdBi system, where R = rare earth element has shown that large room temperature electrical power factors are possible within this family. These compounds were prepared by melting in sealed Ta ampoules and subsequently heat treated. They exhibit p-type

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conductivity, as shown in Fig. 6. which displays the room temperature Seebeck coefficient vs.Lanthanide atomic number.
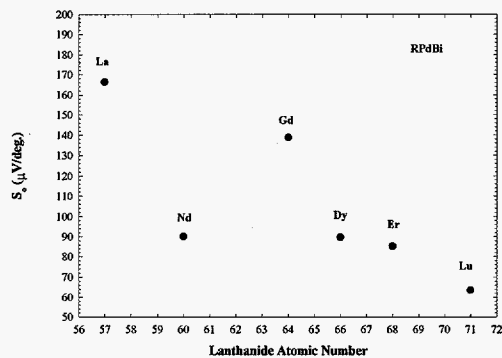

Fig. 6. Room Temperature Seebeck Coefficient of RPdBi Compounds as a Function of Atomic Number.
(R = Rare Earth)
(The LaPdBi sample was not single phase)

The variation of Seebeck coefficient with atomic number is believed to be related to the number of unpaired 4f electrons in the lanthanide valence shell. The anomalous value for the La compound is not fully understood but is likely due to the presence of additional phases. A preliminary screening of the room temperature properties of these compounds indicate that some have room temperature power factors on the order of 30 μW/cm-deg.^{2} or higher. A summary of some of these properties is given in Table II.

Table II. Room Temperature
Properties of RPdBi
(R=Rare Earth)

Compound	ρ (mΩ-cm)	S_o (μV/°C)	PF_o (μW/cm-°C^2)
LaPdBi	1.0	166.4	27.7
NdPdBi	1.8	90.2	4.5
GdPdBi	0.5	138.8	38.5
DyPdBi	2.0	89.8	4.0
ErPdBi	0.7	85.3	10.4
LuPdBi	1.1	63.6	3.7

Most of these compounds, however, have an energy gap on the order of 0.1 eV or less which would suggest that the Seebeck coefficient, and hence the power factor, would both decrease with increasing temperature. A few of these, particularly LaPdBi and GdPdBi, may, however, be attractive candidates for thermoelectric

cooling applications. Other compounds known to crystallize in the MgAgAs structure that may have semiconducting properties include the RPtSb system where R is a heavy rare earth element. Little transport data has been measured on these compounds to date.

Conclusions

Intermetallic compounds having a gap in the density of states at the Fermi level are attractive candidates for low and intermediate temperature thermoelectric applications. Preliminary transport measurements on annealed TiNiSn indicate that electrical power factors exceeding 25 μW/cm-°C^2 within the 300°C to 600°C temperature range are achievable. Control of microstructure is a critical processing variable in the optimization of these alloys.

Acknowledgment

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