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Thermoelectric properties of ternary and Al-containing quaternary $Ru_{1-x}Re_xSi_y$ chimney–ladder compounds

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Abstract

The thermoelectric properties of ternary and Al-containing quaternary $Ru_{1-x}Re_xSi_y$ chimney–ladder phases have been studied as a function of the Re concentration with the use of directionally solidified alloys. The $Ru_{1-x}Re_xSi_y$ chimney–ladder phases exhibit n- and p-type semiconducting behaviors, respectively, at low and high Re concentrations, at which the X(=Si)/M(=Ru + Re) ratios are respectively, larger and smaller than those expected from the VEC (valence electron concentration) = 14 rule. The absolute values of both Seebeck coefficient and electrical resistivity increase as the extent of the deviation from the VEC = 14 rule increases, i.e. as the alloy composition deviates from that corresponding to the p–n transition ($x \approx 0.5$), indicating that the carrier concentration can be controlled by changing the extent of compositional deviation from the ideal VEC = 14 composition. The highest values of the dimensionless figure of merit obtained are 0.47 for ternary ($x = 0.60$) and 0.56 for Al-containing quaternary alloys. The reasons for the systematic compositional deviation from the ideal VEC = 14 compositions observed for a series of chimney–ladder phases are discussed in terms of atomic packing.

Keywords: Transition metal silicides; Thermoelectric; Crystal structure; Electron diffraction; Semiconductor compounds

1. Introduction

Ruthenium sesquisilicide (Ru_2Si_3) has been considered as a promising candidate for a high-temperature thermoelectric material because of its high Seebeck coefficient and low thermal conductivity [1–14]. Ru_2Si_3 crystallizes into two different types of structures: a tetragonal-type high-temperature (HT) phase and an orthorhombic-type low-temperature (LT) phase [15]. The HT-Ru_2Si_3 phase is a member of a family of materials known as the Nowotny "chimney–ladder" phases [15]. The chimney–ladder phase generally formulated to be M_nX_{2n-m} has a structure composed of subcells of transition metal (M) atoms in a tetragonal β-Sn arrangement ("chimney") and group 14 or 13 atoms (X) in a coupled helical arrangement ("ladder"), with both the chimney and the ladder being aligned along the *c*-axis of the tetragonal unit cell, where *n* and *m* indicate, respectively, the numbers of M and X subsells in the unit cell of a given chimney–ladder phase [16–20]. Extensive studies on various chimney–ladder phases have revealed that most chimney–ladder phases tend to satisfy a valence electron concentration rule, i.e. they are stabilized when the valence electron concentration per transition-metal atom (VEC) is equal to 14. Under this circumstance, the Fermi energy of the chimney–ladder phases is located in the middle of a narrow band gap so that they exhibit semiconducting properties [7,19–21]. The semiconducting nature, together with low thermal conductivity originating from the complex crystal structure, makes the chimney–ladder phases, including HT-Ru_2Si_3, attractive as possible thermoelectric materials [3].

Since the chimney–ladder phases are electron compounds following the VEC = 14 rule, the crystal structure and therefore the intrinsic physical properties are expected

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to be controlled by alloying with a substitutional element, especially when the number of valence electrons of the alloying element is different from that of the constituent element [16–20]. Recently, we have studied the phase relationship in the Ru–Re–Si systems using polycrystalline samples produced by arc-melting and found that the HT-Ru_2Si_3 phase with the chimney–ladder structure is stabilized to appear at low temperatures by the partial substitution of Ru atoms (group 8) with Re atoms (group 7) [11]. A series of $Ru_{1-x}Re_xSi_y$ chimney–ladder phases exists roughly along the composition line connecting two end binary phases satisfying the VEC = 14 rule, namely Ru_2Si_3 and Re_4Si_7, in the Ru–Re–Si ternary phase diagram over a wide compositional range of $0.14 \leqslant x \leqslant 0.76$. However, the observed $x - y$ relation for the $Ru_{1-x}Re_xSi_y$ chimney–ladder phase was found to deviate systematically from the relation expected from the VEC = 14 rule, i.e. $y = 1.5 + 0.25x$. The actual composition line was determined to be $y = 1.539 + 0.178x$ ($Ru_{1-x}Re_xSi_{1.539+0.178x}$) [11]. The compositional deviation from the composition satisfying the VEC = 14 rule is expected to be used to predict the semiconducting properties of the chimney–ladder phases, when referring to the calculation by Imai and Watanabe [22] and Migas et al. [21].

The compositional deviation from the VEC = 14 rule for Re-poor $Ru_{1-x}Re_xSi_y$ chimney–ladder phases occurs in such a way that more Si atoms exist than the VEC = 14 rule predicts, so that these chimney–ladder phases exhibit n-type conducting behavior due to the existence of additional electrons [11]. On the other hand, the compositional deviation from the VEC = 14 rule for Re-rich $Ru_{1-x}Re_xSi_y$ chimney–ladder phases occurs in such a way that fewer Si atoms exist than the VEC = 14 rule predicts, so that these chimney–ladder phases exhibit p-type conducting behavior [11]. The p–n transition is predicted to occur at $x \approx 0.5$ from the change in the sign of the compositional deviation from the VEC = 14 rule.

Our preliminary measurement of the Seebeck coefficient with the use of polycrystalline alloys has indicated that $Ru_{1-x}Re_xSi_y$ chimney–ladder phases exhibit n- and p-type semiconducting behaviors when the alloy compositions are Re-poor and Re-rich, respectively [11]. However, since the extent of the compositional variation in the chimney–ladder phases observed in the polycrystalline specimens produced by arc-melting is quite large (the difference in the Re content in chimney–ladder phases for a given specimen is usually as large as 15–20%), the exact composition for the p–n transition has not yet been confirmed experimentally. This has to be clarified with specimens with less compositional variation in the chimney–ladder phases. In addition, establishing a way to control the compositional deviation from the composition satisfying the VEC = 14 rule is a key factor to providing the chimney–ladder phases with desirable thermoelectric properties through not only changing the type of carrier but also their concentrations. It is thus important to elucidate the origin of the compositional deviation from the ideal value satisfying the VEC = 14 rule. Although many studies on some chimney–ladder phases have been carried out so far to explain why they are formed so as to maintain the VEC = 14 rule [19,20,23], the reasons for the compositional deviation observed for most of the chimney–ladder phases, especially when large amounts of substitutions are made, have not been studied in detail.

In the present study, we investigate the thermoelectric properties of the $Ru_{1-x}Re_xSi_y$ chimney–ladder phases as a function of the Re content (x in $Ru_{1-x}Re_xSi_y$), i.e. as a function of the sign and amount of compositional deviation from the ideal value satisfying the VEC = 14 rule, with the use of directionally solidified alloys for which less compositional variations are expected to occur in the chimney–ladder phases, in order to gain insight into the reasons for the compositional deviation. We also investigate the effects of Al additions on the thermoelectric properties and the compositional deviation of the $Ru_{1-x}Re_xSi_y$ chimney–ladder phases in order to see whether the compositional deviation from the ideal value satisfies the VEC = 14 rule, and thus whether their physical properties can be further controlled by quaternary alloying.

2. Experimental procedure

Rod ingots of ternary $Ru_{1-x}Re_xSi_{1.54+0.18x}$ alloys with $x = 0.14$, 0.23, 0.36, 0.53, 0.60 and 0.73 and quaternary $Ru_{0.27}Re_{0.73}(Si_{1-\delta}Al_\delta)_{1.67}$ alloys with $\delta = 0.04$, 0.08 and 0.16 were produced by arc-melting elemental Ru (3N-grade), Re (4N-grade), semiconductor-grade Si and Al (4N-grade) in an Ar atmosphere. For Al-substituted alloys, the Re/M ratio was fixed at 0.73, which is close to the solubility limit of Re in the chimney–ladder phases of the Ru–Re–Si ternary system. These ingots were directionally solidified in an optical floating zone (FZ) furnace at a growth rate of 5.0 mm h^{-1}. The microstructures of as-grown crystals were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Chemical compositions for selected regions of interest in as-grown crystals were estimated by energy-dispersive X-ray spectroscopy (EDS) in SEM and TEM. The Al/Si ratios for the Al-substituted samples were estimated by wavelength-dispersive X-ray spectroscopy (WDS). Lattice constants of the metal sublattice of chimney–ladder phases were examined by powder X-ray diffraction. Specimens for TEM observations were prepared by mechanical polishing, dimple grinding and finally Ar-ion milling at 4 kV for electron transparency.

Rectangular specimens with the approximate dimensions of $2 \times 2 \times 7$ mm^3 were cut from directionally solidified ingots by electric discharge machining for measurements of the Seebeck coefficient and electrical resistivity. Measurements of the Seebeck coefficient and electrical resistivity were made with our ULVAC ZEM-2 apparatus in the temperature range from 173 to 973 K at intervals of 50 K, with measurement errors of less than ±7 and ±10%, respectively. Values of thermal conductivity