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Improvement of thermoelectric power of n-type earth-abundant iron rich alloy by microstructure engineering

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ABSTRACT

Due to the exhaustion of rare metal resources and the hazard of toxic material to the environment, development of cost-effective, nontoxic, and earth-abundant thermoelectric materials has become more urgent. This study introduces a nontoxic, earth abundant n-type iron-based cost-effective Fe–2.3C–Si–5Mn–7V–8Cr thermoelectric material that is prepared by a simple melting method. Significant increase in both electrical conductivity and Seebeck coefficient are achieved by several heat treatment processes to optimize the distribution and grain size of VC, $Cr_{23-x}Fe_xC_6$ typed chromium carbide as well as base matrix. As a result, the power factor of the sample that is normalized at 1150 °C is about 0.75 $mWm^{-1}K^{-2}$ in maximum value, which is 2.6 times larger than that (0.29 $mWm^{-1}K^{-2}$) of as-cast sample. The highest *ZT* value of the sample that is normalized at 1150 °C is 0.028 at 868 K, which is 4.3 times larger than that of as-cast sample (0.0065 at 964 K) in present study, indicating that a proper heat treatment process would remarkably enhance *ZT* value. This research provides extremely valuable data for the future researches on thermoelectric alloys.

1. Introduction

Thermoelectric materials have drawn much attention because they can be used for direct and reversible conversion of heat into electrical energy. Efficient thermoelectric materials are often characterized by their high the thermoelectric dimensionless figure of merit, *ZT* value. According to the equation $ZT = S^2\sigma T/k$ (where S, σ, k and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and working temperature, respectively), high *ZT* value can be obtained by increasing S, σ as well as decreasing k.

The bulk oxide materials such as $SrTiO_3$-based materials have their special merits including good thermal stability, environment friendly, economical preparation process and variety of chemical compositions. However, *ZT* value of these materials is still low (0.37 in highest value) [1]. Although some alloy materials such as Bi_2Te_3 [2,3], Zn_4Sb_3 [4] and $Cu_{2-x}Se$ [5] have shown high-thermoelectric performance with the *ZT* values ranging from 0.8 to 1.5, the usages of rare or toxic elements in these compounds are problematic from the point of view of environmental protection. For large-scale commercial application, the cost effectiveness, nontoxicity and earth abundance should be taken into account for high performance thermoelectrics.

As an environmentally friendly material, Iron (Fe) is one of the most common nontoxic metal elements with large storing capacity on the earth. From this point of view, Iron (Fe) would be the most promising thermoelectric material because of its abundance as well as low cost and simple production process.

First-principles electronic structure and Boltzmann transport calculations have been utilized into the research on thermoelectric properties of iron-based alloys to obtain a high Seebeck coefficient value from a theoretical aspect [6].

Many researches have focused on the p-type iron-based alloys [7–10], including Fe–Si alloys [9] and Fe–V–Ti–Ta–Al alloys [10] which have relatively higher Seebeck coefficient (25–250 $\mu V K^{-1}$). On the other hand, there are many literature for n-type iron-based alloys [9,11–13]. For example, Co doped n-type Fe–Si alloy [9] has large Seebeck coefficient (about −60

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to −170 μVK^{-1}), and its low electrical conductivity (80–200 Scm^{-1}) resulted in a much lower power factor (~0.45 mWm^{-1}K^{-2}). Further, there still has some n-type alloys possessing low Seebeck coefficient [12,13]. Accordingly, there is a compelling need to optimize Seebeck coefficient and electrical conductivity of n-type iron-based alloys for high thermoelectric performance.

The power factor ($PF = S^2\sigma$) can be enhanced by energy filtering effect [14]. Since the grain-boundary potential barriers passes the high energy carriers and block the low energy carriers, Seebeck coefficient increased by energy filtering effect on grain-boundary potential barriers [15]. Meanwhile, the thermoelectric performance is improved by energy filtering effect [16], multilevel phonon scattering behaviors [17] and grain boundary phonon scattering [3]. This mechanism would provide a potential application on iron-based alloys.

Based on the concept of design of thermoelectric iron-based alloys [11,18,19], we selected the elements of C, V, Cr, Si and Mn to prepare an n-type iron-based Fe–2.3C–Si–5Mn–7V–8Cr alloy by direct melting method in induction furnace followed by different heat treatment processes. C, V, Cr can be precipitated in the form of VC and $Cr_{23-x}Fe_xC_6$ type chromium carbide [20]. Upon adding Mn (belongs to VIIB) and Si (belongs to IVB) which are placed at right side of Vanadium, the total number of valence electron can be enhanced [21], resulting in a minus Seebeck coefficient. The correlations among Seebeck coefficient, electrical conductivity and microstructure are discussed.

2. Methods

Fe–2.3C–Si–5Mn–7V–8Cr alloys (with composition of C ~ 2.3Wt%, Si ~ 1.0Wt %, Mn ~5.0Wt%, Cr ~8.0Wt%, V ~ 7.0Wt%) were prepared in an induction melting furnace in an ambient environment, which is simple and inexpensive approach compared to previously reported thermoelectrics preparation methods. The as-cast alloy was obtained at the temperature of 1750 °C by adding vanadium and chromium to crystallize vanadium spheroidal carbides and lamellar chromium carbides in the austenitic structure. Then, three sorts of heat treatment process were performed on the alloys, i. e. annealing at 1000 °C, normalizing at 1150 °C and 1200 °C, respectively.

X-ray diffraction (XRD, D/MAX-2500, Rigaku) method and scanning electron microscopy (SEM, Quanta FEG, FEI) were employed to observe morphology and size of ingredients of microstructure. Energy Dispersive Spectrometer (EDS, OXFORD X-MAX^{N}) was used to analyze chemical composition and retained flux in product.

The Seebeck coefficient and electrical conductivity were measured at temperature range of 303–1063 K in He atmosphere by thermoelectric measuring apparatus (LRS-3, Linseis, Germany). The thermal diffusivity (α) at temperature range of 323–809 K was measured by a discovery xenon flash (DXF-500, TA instruments, USA) on the dish samples. The specific heat capacity (C_p) was measured by differential scanning calorimeter (DSC 200 F3, Netzsch, Germany). Thermal conductivity at temperature ranging 323–809 K was calculated from the specific heat capacity, thermal diffusivity and experimental density (ρ = 7.42 g/cm^3) by using the equation, $k = \alpha C_p \rho$. The thermal conductivities of samples at above 809 K were approximated by the least square method.

3. Results

Fig. 1 illustrates the X-ray diffraction (XRD) patterns, crystal structures and Scan Electron Microscope- Energy Dispersive Spectrometer (SEM-EDS) analyzed images of as-cast alloy and three

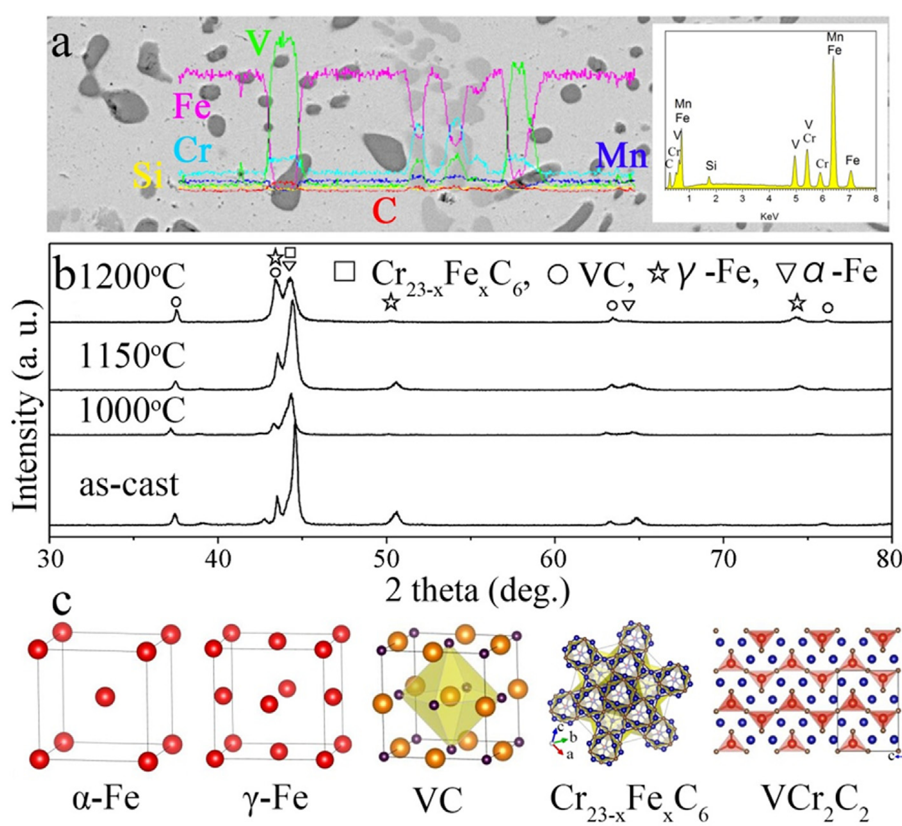

Fig. 1. SEM-EDS analyzed images (a), X-ray diffraction (XRD) patterns (b) and crystal structures (c) of samples.