Journal of Alloys and Compounds 690 (2017) 652–657

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Microstructure and thermoelectric properties of WSi_2-added $CrSi_2$ composite

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ARTICLE INFO

Article history:
Received 3 February 2016
Received in revised form
3 August 2016
Accepted 18 August 2016
Available online 20 August 2016

Keywords:
Thermoelectric materials
Silicide
Composite materials
Powder metallurgy

ABSTRACT

$CrSi_2$-based composite materials with submicrometer-sized grains were fabricated by the powder metallurgical process using ball-milling and pulse-current sintering. By the solid-state reaction of submicrometer-sized fine powders of $CrSi_2$ and WSi_2 during the sintering, the composites consisting of Cr-rich hexagonal $(Cr,W)Si_2$ phase and W-rich tetragonal $(W,Cr)Si_2$ phase were obtained. The grain size of $CrSi_2$ phase was effectively reduced by the WSi_2 addition because of the suppression of grain growth during sintering. Thermal conductivity was then decreased with the WSi_2 content by the enhancement of phonon scattering resulting from the reduction of grain size, the introduction of the $CrSi_2/WSi_2$ interface and the crystal lattice distortion induced by the W substitution for $CrSi_2$ phase. Seebeck coefficient and electrical resistivity were also decreased due to the addition of metallic WSi_2 phase and the deformation of $CrSi_2$ electronic structure resulting from the W substitution. The WSi_2 addition had then little effect on the thermoelectric power factor. Consequently, the thermoelectric figure-of-merit, ZT, was enhanced by the reduction of thermal conductivity and reached 0.3 around 700 K.

1. Introduction

Thermoelectric devices have recently attracted renewed interest in their potential application to clean energy-conversion systems. In particular, energy recovery from vast amounts of waste heat are targeted for thermoelectric power generation because the temperature and the energy scale of most heat sources are too low to reuse efficiently with other conventional energy conversion systems. The conversion efficiency of thermoelectric devices depends mainly on the thermoelectric performance of the material, which is evaluated using the thermoelectric figure of merit, $ZT = (S^2/\rho\kappa)T$, where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature. The telluride materials, such as Bi-Te or Pb-Te system, exhibit relatively high ZT values and are suited for thermoelectric power generation devices. However, it seems to have run into difficulty for widespread use because of its higher cost and the limited supply of raw materials, especially Te.

Transition metal silicides have been studied intensively for thermoelectric application because of its abundance of raw material, low toxicity and high chemical stability. Chromium disilicide, $CrSi_2$, is one of the promising silicide because of its large S and low ρ, resulting in large power factor, PF ($=S^2/\rho$), over 1 mW/mK^2 above room-temperature [1–4]. In addition, the high oxidation resistance in air up to 900 K [5] is a favorable property for the long-term stability as a thermoelectric power generation device. However, the relatively high intrinsic κ value of $CrSi_2$ of over 12 W/mK [4] limits its ZT value to ~0.2. The reduction of κ is therefore necessary for efficient thermoelectric power generation.

Since κ in the $CrSi_2$ system is mainly governed by the lattice part of κ, the enhancement of phonon scattering should be effective to reduce total κ value. Indeed, κ value was effectively decreased by the structural refinement, such as the reduction of grain size [3,4]. In this study, $CrSi_2$-based composites were fabricated by the addition of WSi_2. For the selection of additive material, the low ρ and crystallographic compatibility are desirable in order to avoid the degradation of electrical conductivity by the formation of composite. In addition, the high chemical stability in $CrSi_2$ matrix is also required. From these aspect, metallic or semimetallic silicide materials seem to be promising candidate as the additive material for $CrSi_2$. However, since the 3d transition silicides or the homologous molybdenum silicide easily form a solid solution with $CrSi_2$ [2,6,7], it is difficult to obtain the stable composite structure. Therefore, WSi_2 having a limited solid

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http://dx.doi.org/10.1016/j.jallcom.2016.08.185
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solubility for $CrSi_2$ was chosen as an additive material in this study.

The composites consisting of submicrometer-sized fine grains were prepared by the powder metallurgical process using ball-milling and pulse-current sintering in order to enhance the phonon scattering at grain boundaries. In addition, the heavy-element W doping effect on the $CrSi_2$ crystal structure, which is also effective for the reduction of κ by the mass-difference scattering in the crystal lattice, was investigated. It was found that the appreciable reduction of κ by the WSi_2 addition without a serious deterioration of electrical aspect of thermoelectric property improved the ZT value of the $CrSi_2$-based material.

2. Experimental

$CrSi_2$-based composite materials with the nominal composition of $(CrSi_2)_{1-x}(WSi_2)_x$ ($x = 0.02–0.10$) were fabricated by the powder metallurgical process. Commercially available $CrSi_2$ (99%, Rare Metallic Co., Ltd.) and WSi_2 (99%, Rare Metallic Co., Ltd) powders were used as the raw material. Although the purity of these raw materials was rather low, almost all impurity materials are oxides, which are usually stable in silicide. Therefore, it can be expected that the effect of impurity phase on thermoelectric properties of samples is negligible. Appropriate amounts of $CrSi_2$ and WSi_2 powders were mixed and milled in a planetary ball mill (FRITSCH GmbH, PULVERISETTE 5/4) with a 500-ml-capacity Cr steel pot and carbide balls. In the milling system, the pot rotates on its axis against the direction of orbital motion. The pot was back-filled with a purified Ar gas atmosphere after creating a vacuum. A total mass of 800 g of 5-mm-diameter WC balls was inserted with 30 g of mixed powder into the pot. The ball-milling was performed at 250 rpm for 10 h with a 10 min rest every half-hour. After the ball-milling process, well-mixed and finely-pulverized powders with submicrometer-size were obtained. The prepared powder was sintered using pulse-current sintering (PCS). The powder was put into a graphite mold and sintered at 1373 K for 10 min in vacuum under a uniaxial pressure of 50 MPa. The heating and cooling rates were 100 K/min. For comparison, $CrSi_2$-only sintered samples were also prepared from the raw $CrSi_2$ powder with an average particle size of several μm and from the as-milled $CrSi_2$ powder synthesized by the same ball-milling process. The obtained bulk samples, with a typical size of 10 mm in diameter and 2 mm in thickness, were used to measure κ and then cut into a bar shape with a typical size of $2 \times 2 \times 9$ mm^3 to measure ρ and S.

Crystalline phase analysis was performed using X-ray diffraction (XRD) with Cu Kα radiation. Microstructural observation and compositional analysis was conducted using the scanning electron microscopy (SEM) and the attached energy dispersive X-ray spectrometry (EDX). S and ρ were simultaneously measured in a He atmosphere. ρ was evaluated by a conventional four-probe DC technique. S was calculated from a plot of the thermoelectric voltage versus the temperature difference. κ was evaluated from the density (D), thermal diffusivity (α), and heat capacity (C_p) with the relationship $\kappa = D \times \alpha \times C_p$. D was measured using the Archimedes method, and α and C_p were evaluated using the laser flash method.

Density functional theory was performed based on the linearized augmented plane wave method using Wien2k code [8]. For the pure $CrSi_2$, experimental structure was adopted, while the structural optimization was carried out for W doped $CrSi_2$. Here, doping was performed to the super cell structure of $1 \times 1 \times 2$, and chemical composition was fixed to the Cr_2WSi_6 in which doping site was selected to the Cr (1/2, 1/2, 1/3) in the super cell. The number of k-point in the Brillouin zone of 2560, the size of basis set (rkmax) of 8.0, and the exchange-correlation functional of generalized gradient approximation were adopted. The calculation self-converged within the energy of 0.1 mRy.

3. Results and discussion

The XRD measurement was performed on the cross-section of sintered $(CrSi_2)_{1-x}(WSi_2)_x$ composites to investigate the relation between the composition x and the crystal structure of the obtained samples. As shown in Fig. 1, the stoichiometric $CrSi_2$-only sintered sample made from the as-milled powder formed a *C*40 hexagonal structure with space group of $P6_222$ as reported in the literature. Although no trace of an impurity phase, such as oxides, was detected, weak diffraction perks from chromium monosilicide CrSi was observed. The Rietveld analysis had revealed that the presence of a secondary phase of the CrSi phase at 2.7 at%. In addition, the CrSi phase was also observed in every composite samples around 3 at%. However, it is reasonable to assume that the secondary phase could not disturb the investigation of WSi_2 addition effect on $CrSi_2$ phase because the CrSi phase was present in every samples at an almost constant proportion. For the composite samples, diffraction peaks from $CrSi_2$ phase tend to monotonically shift toward the lower 2θ angle with the amount of WSi_2 content. The lattice parameter of $CrSi_2$ phase calculated from the 2θ angle of diffraction peaks then increased with the amount of the WSi_2 addition, as shown in Fig. 2. This tendency reflects that the crystallographic structure of $CrSi_2$ phase was enlarged by the partial substitution of W, which has a larger atomic radius than Cr. In addition, diffraction peaks from the tetragonal WSi_2 phase were detected in $x \geq 0.04$, as shown in Fig. 1. Moreover, the peak position was slightly higher than that of the WSi_2 powder, which was used as a raw material. Although it is difficult to precisely calculate lattice parameter from these weak diffraction peaks, this result implies that the W site in the WSi_2 phase was also partially substituted by Cr having the smaller atomic radius, resulting in the shrinkage of

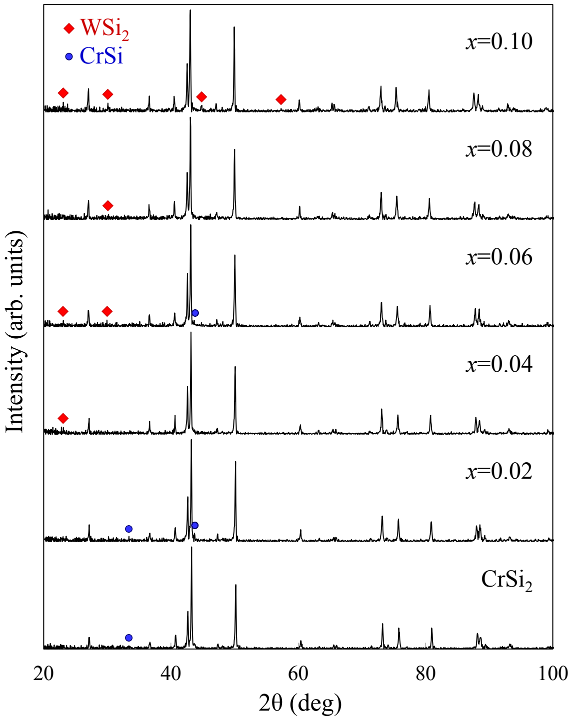

Fig. 1. XRD patterns (Cu Kα radiation) diffracted from the $CrSi_2$ sintered sample made from the milled powder and sintered composites with the nominal composition of $(CrSi_2)_{1-x}(WSi_2)_x$.