SEM/EDS/EBSD study of the behaviour of Ge, Mo and Al impurities in complex-doped crystals of higher manganese silicide

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Abstract. The structure of Al, Ge, Mo doped higher manganese silicides (HMS) grown by the Bridgman technique has been studied by SEM/EDS/EBSD methods. It is shown that dopants are partially integrated into the HMS crystal lattice. Some inclusions with sizes of 0.1-100 µm and different shapes (round, irregular, elongated) are formed. The precipitation of tetragonal MoSi₂ and Si-Ge solid-solution has been observed. MoSi₂ inclusions hundreds of microns in size form a multicomponent texture. The inclusions of Si-Ge solid solution have an irregular shape. The orientation relationship between these inclusions and matrix crystal is determined.

1. Introduction

Higher manganese silicides (HMS) of stoichiometry MnSi₁.₇₁-₁.₇₅ attract the attention as potential middle-temperature thermoelectric materials which are rather cheap and non-toxic [1-3]. There are four phases with approximate composition Si/Mn=1.7 corresponding to HMS. The HMS has a figure of merit of $ZT=\alpha^2\sigma T/\kappa \approx 0.4$ ($\alpha$ – Seebeck coefficient, $\sigma$ – electrical conductivity, $\kappa$ – thermal conductivity, $T$ – absolute temperature).

As a rule, when HMS crystal was grown by the Czochralsky or Bridgman technique the ordered precipitation of MnSi cubic phase (striations) has been observed [4, 5]. The MnSi phase is a good conductor with high thermal conductivity, thus it causes the degradation of HMS figure of merit [6]. The possible way to improve thermoelectric properties is doping. Aoyama et al. [7] showed that Ge doped HMS crystals possessed higher $ZT$ value, and the microstructure of doped crystals was changed. MnSi cubic phase was not revealed. Al impurity has been shown to increase the HMS figure of merit [8]. Mo reduces the lattice component of thermal conductivity [9]. The most significant increase in the figure of merit is observed with combined doping by Ge, Mo and Al [2, 8]. However, there is not enough information about the microstructure of doped HMS crystals. The aim of this work is to reveal structural features of complex doped HMS crystals.
2. Materials and methods

A complex doped HMS crystal of nominal composition \((\text{Mn}_{0.98}\text{Mo}_{0.02})[(\text{Si}_{0.98}\text{Ge}_{0.02})_{1.75}]_{0.99}\text{Al}_{0.01}\) was grown by modified Bridgman method described in detail in [8]. Advanced electron microscopy techniques were applied for characterization of elements distribution in matrix crystal. Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS) and Electron Backscattered Electron Diffraction (EBSD) were used for morphology and microstructure investigation as well as for chemical analysis, phase composition study and texture analysis. A dual-beam scanning electron microscope FEI Quanta 200 3D equipped with X-ray EDS and EBSD detectors (EDAX, Ametek) was used.

The samples were prepared by mechanical polishing with diamond lapping films (grain size down to 0.5 µm). For EBSD technique the final step was the mechanical polishing by \(\text{Al}_2\text{O}_3\) colloidal suspension with grain size of 50 nm. The upper disordered layer was removed by \(\text{Ar}^+\) ion milling.

3. Experimental Results

3.1 SEM / EDS data

Analysis of SEM images of the complex-doped HMS crystal does not reveal any ordered precipitates of MnSi phase. However, the matrix crystal contains inclusions with sizes of 0.1-100 µm that have different shapes (round, irregular, elongated) and compositions (Fig. 1).

In accord with EDS microanalysis data obtained at 15 keV the manganese/silicon ratio in the doped matrix crystal is 1.7. This ratio corresponds to HMS composition. The dopants observed at concentrations above detection limits were Al and Mo (0.5 ± 0.3 at%) and Ge (1.5 ± 0.4 at%).

![Figure 1](image)

**Figure 1.** Backscattered SEM image of complex-doped higher manganese silicide crystal

The elemental distribution analysis reveals Si-Ge and Si-Mo inclusions are present in the sample. The EDS map of Al distribution coincides with O map, thus it can be supposed that alumina is formed. The Si-Ge solid-solution inclusions have irregular shape with different ratios of elements. In accordance with microanalysis data, two types of Si-Ge inclusions are present - Ge-rich and precipitates with composition close to SiGe. The first one consist of ~ 90 at% Ge and the second one have a ratio of Si:Ge = 1:1 in the central part and are Ge-rich at the boundary. In addition, separate faceted Mo-containing inclusions hundreds of microns in size are also observed, with a Mo:Si ratio of 1:2. These inclusions were revealed only in a separate area of matrix crystal, while Si-Ge inclusions of both types were homogeneously distributed.
3.2 EBSD data

The EBSD study revealed three types of EBSD patterns from different micro-areas in Fig. 2. They are indexed with low fit factor (it varies from 0.2 to 0.4) and high confidence index (0.7-0.9). The diffraction pattern (DP) from matrix crystal is indexed as tetragonal crystal lattice $\text{Mn}_4\text{Si}_7$ with space group $\text{P}4_2$ and unit cell parameters $a=0.553$ nm and $c=1.752$ nm [10] (Fig. 2a). This is one of four known phases of higher manganese silicides. The analysis of 350,000 DPs obtained from an area 2000 µm x 3000 µm in size revealed grain structure of matrix crystal. The grains consist of several millimeter large blocks misoriented to each other by ~2 degrees.

The DPs from Si-Ge inclusions were indexed as cubic crystal lattice with space group $\text{Fd}m$ and unit cell parameter $a=0.53$ nm [11], with experimental error ~1% (Fig. 2b). The Si-Ge solid-solution inclusions of both types have a similar single crystal structure. These inclusions are oriented relative to the matrix crystal as (121)[100]$\text{Si-Ge}$ || (010)[100]$\text{Mn}_4\text{Si}_7$. Also, a few polycrystalline inclusions of Ge-rich type are observed.

![Figure 2](image.png)

**Figure 2.** EBSD diffraction patterns from (a) matrix crystal, (b) Si-Ge solid-solution inclusion and (c) Mo-containing precipitates.

The experimental Kikuchi diffraction pattern from inclusions with Mo:Si=1:2 ratio (Fig. 2c) is in a good agreement with simulated DP for tetragonal MoSi$_2$ phase (space group $I4/mmm$, cell parameters $a = 0.32$ nm and $c = 0.78$ nm [12]). These inclusions have a large-scale polycrystalline grain structure. The preferred orientation of these inclusions has been examined in the approximation of "one grain - one orientation" to exclude the influence of the size factor. The texture analysis is made along [001] $\text{Mn}_4\text{Si}_7$ zone axis of the matrix crystal because it is the main direction relevant for thermoelectric
properties (Fig. 3). Inverse pole figure analysis reveals three maxima corresponding to (110), (118) and (507) planes (Fig. 3b).

Figure 3. Inverse pole figure (a) of (001) orientation of Mn₄Si₇ matrix crystal and (b) colour coded texture analysis data of MoSi₂ inclusions.

The weight of each preferred orientation was estimated ±5º area around maxima. Weight fractions are 0.25 for (118), 0.35 for (110) and 0.40 for (507) plane. Thus, we can conclude that along [001] Mn₄Si₇ direction MoSi₂ inclusions form a multicomponent texture.

4. Conclusions

The microstructure of complex doped crystals of higher manganese silicide has been studied by several methods. EDS microanalysis reveals the manganese/silicon ratio in the doped matrix crystal is ~1.7, which corresponds to a HMS composition of \((\text{Mn}_{0.98}\text{Mo}_{0.02})[(\text{Si}_{0.98}\text{Ge}_{0.02})_{1.75}]_{0.99}\text{Al}_{0.01}\). The Al, Mo, Ge dopants are present in following concentrations: ~0.5±0.3 at% Al and Mo and ~1.5±0.4 at% Ge. Addition of Al, Ge, Mo leads to the formation of Si-Ge and MoSi₂ inclusions. MnSi ordered striations typical of undoped HMS crystals are not observed.

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