X-Ray Study of Interfacial Interactions in Highly Milled Sn-Ge Powders

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ABSTRACT

We have studied possible structural changes occurring at the Sn/Ge interface of highly milled Sn/Ge composites. EXAFS and X-ray Diffraction measurements were made on mechanically milled powders having compositions ranging from 20 to 50 vol.% Sn. X-ray diffraction measurements indicate the increasing amorphization of Sn as the Sn content is decreased. EXAFS results indicate that this amorphous phase is due to the formation of an α -Sn/Ge alloy. The EXAFS from this alloy did not change significantly at the Sn melting point. X-ray diffraction measurements made at room temperature show a systematic decrease in the intensity of Sn peaks and broadening of Ge peaks with the decreasing Sn content.

INTRODUCTION

Recently Jang and Koch[1,2] by their x-ray diffraction and DSC studies on mechanically milled Sn/Ge powders have made some interesting observations. They have seen the possible depression of the melting point and broadening of the melting transition region of Sn with decreasing Sn content. Also when the Ge volume reaches a value where essentially all the Sn atoms are adjacent to the Ge particle surfaces, the Sn is said to be in a disordered, perhaps in an amorphous, state such that no melting transition is observed. According to the simple eutectic Ge-Sn equilibrium diagram there is essentially no solid solubility of Ge in Sn and very small (< 1 at. %) solubility of Sn in Ge. It is interesting to see whether there is another phase of Sn, namely the cubic form α -Sn, as it reaches this disorderd state. It is known that Ge can stabilize the α -Sn phase.[3] The motive behind our work is to identify this so called disordered phase or form structurally, using Extended x-ray absorption fine structure (EXAFS) which is a proven tool to study disordered materials because of its ability to investigate the local atomic structure of each of the components in a material. X-ray diffraction and Differential Scanning Calorimetry have also been used to support our results. In this paper we discuss some of the results we have obtained recently.

EXPERIMENTAL

Sn/Ge powder samples were made using a Brinkmann, Model MM2, Standard Mixer Mill operated in an Ar ambient. Powders (-100 mesh, 99.999% pure) were milled in a sealed hardened tool steel vial, using a steel ball. Loading and unloading of powders to the vial were done inside a dry box with moisture and oxygen content of < 5 ppm. Powders with varying Sn/Ge volume ratios (20, 30, 40 and 50 vol.% Sn) were milled for nearly a constant time of about 32 hours. Differential Scanning Calorimetric analysis done on these samples produced results similar to those of Jang and Koch.

In order to prepare x-ray samples of proper absorption, the powders were diluted to proper amounts with carbon and packed in an array of slots made in a rectangular Cu plate and sealed in a container which has windows (Kapton) transparent to x-rays. Another sample was packed in a slotted Al plate using thin Al windows to perform the heating experiments. An attempt was made to make an α -Sn standard by melting a piece of regular Sn (β -Sn) with a very small amount of Ge (< 0.5 at. %) in a UHV chamber. In order to initiate the transformation the specimen was kept in a freezer at -30°C . After two days the sample had transformed. It was ground to a fine powder and rubbed onto kapton tape. EXAFS analysis indicated that some of the powder had transformed back to tetragonal β -Sn during the grinding.

EXAFS measurements were made at beamline X-11A at the National Synchrotron Light

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Source. Measurements were made in the transmission mode using a Si(311) double crystal monochromator. Sn K-edge (29200 eV) EXAFS measurements were made at temperatures of 10°K, 100°K and 200°K, in a rough vacuum. One sample (20 vol. % Sn) was heated in a vacuum heating stage above the Sn melting point while measuring EXAFS at several temperatures.

The diffraction measurements were made at room temperature at beamline X-11B using a modified Phillips goniometer with an INEL 120° curved position sensitive detector. This configuration allowed us to acquire a complete diffraction pattern in about 3 minutes.

RESULTS AND DISCUSSION

Figure 1 shows the EXAFS data obtained at 10°K for powder samples of two different compositions namely 50 vol. % Sn and 20 vol. % Sn. We have compared them to the EXAFS of α -Sn (our standard which has some β -Sn contribution) and β -Sn obtained at the same temperature. X-ray diffraction data shows (Figure 2) a decreasing relative intensity of the β -Sn peaks. No new diffraction peaks seem to evolve. This indicates that Sn converts to an amorphous phase. When we measured the EXAFS of the 20 vol. % Sn sample as a function of temperature, it was observed that there was essentially no change in EXAFS (Figure 3) as the sample was heated above the Sn melting point, and the thermal damping was much less than for β -Sn. This indicates that the Sn phase is stable at higher temperatures.

We have analysed our experimental data using EXAFS fitting techniques based on the University of Washington software package. Fourier filtered EXAFS of the samples were used for fitting using a model containing Sn-Sn and Sn-Ge bonds. Measured EXAFS of β -Sn was used as a standard. The contamination of the α -Sn standard with β -Sn made it difficult to use. Therefore, first shell EXAFS corresponding to α -Sn was calculated using the FEFF theoretical code which takes into account the curved wave nature of the photoelectron and multiple-scattering contributions.[4] A similar approach was made to calculate the first shell EXAFS contribution from an ordered α -Sn/Ge alloy which was also used as a Sn-Ge standard in the fitting procedure. Initial results indicate that this

Fig.1 Sn EXAFS data of samples (a) β -Sn (b) 50 vol. % Sn (c) 20 vol. % Sn and (d) α -Sn measured at 10°K.

Fig.2 X-ray diffraction data taken (at 8 keV) at room temperature for samples, (a) 50 vol.% Sn and (b) 20 vol.% Sn. (Peaks with a dot above correspond to β -Sn.)

Fig.3 Temperature dependant EXAFS of 20 vol.% Sn sample. (No significant change in EXAFS amplitude is seen.)

amorphous form is due to the formation of a disordered phase similar to an α -Sn/Ge alloy. Fitting gives a Sn-Sn bond distance of $2.74 \pm .03$ Å and a Sn-Ge bond distance of $2.60 \pm .03$ Å. The Sn-Sn bond distance is similar to that of α -Sn (2.81 Å). If we calculate the lattice parameter of a cubic 50:50 α -Sn/Ge alloy using the corresponding lattice parameters of α -Sn and Ge (6.46 Å and 5.65 Å respectively[5]) we obtain an average near neighbor distance of 2.62 Å which is in reasonable agreement with our fitting result. We can visualize this as an alloy formed by interfacial Sn going into the Ge structure. The alloy:total Sn ratio is found to increase from approximately 40 wt. % to about 100 wt. % with the decreasing Sn content. The broadening of Ge x-ray diffraction peaks (Figure 2) with the decreasing Sn content implies that the decreasing particle size makes more interfacial area available for alloying. XRD line shape analysis shows that the Ge particle size decreases from about 70 nm to about 15 nm when going from 50 to 20 vol. % Sn sample. The observed temperature stability of the 20 vol. % Sn sample above the melting point of bulk Sn may be due to the formation of this alloy. It is reported that the epitaxial films of 50:50 α -Sn/Ge alloys can be grown on Ge substrates at temperatures up to 400°C.[6] This also explains the decrease in melting enthalpy of Sn observed by Jang and Koch as the Sn content is decreased. When essentially all available Sn (when all Sn becomes interfacial) participates in alloying, the melting enthalpy would vanish as they have observed.

To summarize, based on both EXAFS and x-ray diffraction results, the disorder at the Sn-Ge interface may be attributed to the formation of an α -Sn/Ge alloy. The observed stability of this alloy above the melting point of bulk Sn explains the behavior of melting enthalpy of Sn in milled Sn-Ge powders, as the Sn content is decreased.

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