EXAFS Study of Metal-Coated Particles Produced by Ball Milling

Steve M. HEALD, Sumedha JAYANETTI and Kaumudi I. PANDYA

BNL--47545

DE93 002323

Brookhaven National Laboratory, Upton, NY 11973, USA

EXAFS measurements have been carried out on mixtures of Sn with Ge and Si, and Pt with SiO_2 which have been ball milled for extended periods. In these systems the brittle component (Ge, Si, or SiO_2) is ground to nanocrystalline dimensions while the ductile metal is found to coat the outer surface of the particles. Analysis shows that in the Sn-Ge and Sn-Si systems, mixing at the interface is found to form apparently cubic SnGe and SnSi alloys respectively. In the Pt- SiO_2 system while no mixing is observed, the Pt is found to be highly dispersed on the surface of SiO_2 particles.

Keywords: EXAFS, ball milling, Sn, Ge, Si, Pt, SiO_2 , interface, alloying, catalysts

Received
NOV 02 1992
OSTI

1. INTRODUCTION.

High energy ball milling - mechanical alloying or mechanical milling - has recently become a promising method of producing new materials and providing new avenues in materials research. EXAFS measurements made on Sn-Ge powders, milled for extended periods have shown some interesting results.¹ During milling, the ductile component Sn, is found to coat the brittle component Ge, and the resulting mixing at the Sn/Ge interface forms a cubic SnGe alloy of several monolayers thick. For Sn concentration less than 20 vol. % complete incorporation of Sn into the alloy phase is found. The stability of this alloy phase above the bulk Sn melting point explains the previously observed² compositional dependence of the melting enthalpy of Sn in these powders. Similar alloying is observed in the highly milled Sn-Si powders, although it is less extensive compared to that of the Sn-Ge system. This is attributed to the larger lattice mismatch between Sn and Si.

With a view towards possible catalytic applications, we have looked for a similar coating mechanism in ball milled Pt- SiO_2 powders. In the Pt- SiO_2 system no mixing is observed, but both TEM and EXAFS indicate that Pt is highly dispersed on the surface of the SiO_2 particles. The present paper provides a brief discussion of results obtained for all three systems.

2. EXPERIMENTAL.

Sn-Ge, Sn-Si and Pt- SiO_2 samples were milled using a SPEX Industries 8000 mixer/mill operated in an Ar ambient. In each case -100 mesh powders were used as starting materials. The milling container was a sealed cylindrical tool steel vial and the milling media consisted of stainless steel balls as described previously.¹ Powders with varying Sn/Ge (20,30, and 40 vol. % Sn) and Sn/Si (10,25, and 40 vol. % Sn) volume ratios were milled for nearly a constant time of

about 35 hours. Pt- SiO_2 (10 wt. % Pt) powders were milled for about 24 hours.

Sample handling, packing for EXAFS measurements etc. were done inside a dry box with moisture and oxygen content less than 5 ppm. Samples, diluted with Boron Nitride powder to obtain the proper absorption step for EXAFS, were sealed in an airtight copper cell which contains kapton x-ray windows. EXAFS measurements were made at beamline X-11A at the National Synchrotron Light Source (NSLS). Measurements were made in the transmission mode using Si(311) double crystal monochromator, detuned by 20% to reduce harmonics. At the Sn K-edge, and the Pt L_3 edge, the incident and transmitted x-ray beams were monitored using ionization chambers filled with appropriate gases. The Sn edge EXAFS measurements were made at 10 K, 100 K and 200 K, in a displax refrigerator. At the Pt L_3 edge, measurements were made at 80 K.

3. RESULTS AND DISCUSSION.

The EXAFS data of Sn-Ge and Sn-Si showed a systematic change with the decreasing Sn concentration. The corresponding EXAFS Radial Structure Functions (RSFs) showed evolving features indicating that there is another type of bonding in addition to the Sn-Sn bonds with the lowering concentration of Sn. In the Sn-Ge system at 20 vol. % Sn concentration the EXAFS was almost entirely due to this new type of bonding.

The data were analyzed by standard Fourier filtering and non-linear least square fitting method. For Sn-Sn bonds data from Sn powder were used as standards. For Sn-Ge bonds, calculated values obtained using FEFF theoretical code³ (Version 4.08) were used. During calculation the Sn atoms were assumed to be surrounded by four Ge neighbors placed in the zinc blend structure for an alloy with a 50:50 atomic composition. Figure 1 illustrates raw data and a fit obtained for the 20 vol. % Sn sample. A model with both

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Figure 1. (a) Background subtracted k^2 weighted EXAFS and (b) Comparison of filtered data (solid line) to the fit (dashed line) for the 20 vol. % Sn sample.

Figure 2. RSFs for (k^2 weighted, $\Delta k = 16.4-2.81 \text{\AA}^{-1}$) 10 vol.% Sn [Sn-Si sample] (solid line), Sn powder (dashed line), and calculated Sn-Si first shell (dotted line).

Sn-Sn pairs and the Sn-Ge pairs was required in order to attain the best fit. (see Table I) The Sn-Sn contribution was found to be small (approximately 10%) indicating the dominant phase at this concentration to be the SnGe alloy. The number of Ge near neighbors and the bond distance were found to be 2.56 and 2.64 $\text{\AA}$ respectively. The

reduction of the number of near neighbors from the expected value of 4 for a cubic structure can be explained in terms of the existence of the alloy as an interfacial layer around the Ge core particles. The partially coordinated outer layers and disorder are the likely cause for the lowered number of near neighbors. The TEM measurements also show evidence for an alloy layer around the Ge core particles. The bond distance 2.64 $\text{\AA}$ is intermediate between the values for cubic Sn (2.80 $\text{\AA}$) and Ge (2.45 $\text{\AA}$). This indicates that the surface alloy composition contains roughly equal amounts of Sn and Ge, consistent with the film growth observation that the 50:50 composition is preferred.⁴ Recent Mossbauer spectroscopic studies⁵ done on this system also show evidence for interfacial Sn substituted in the cubic Ge structure. X-ray diffraction line profiles indicate that the average Ge particle size is about 250 $\text{\AA}$. Combining this with the EXAFS results gives an alloy layer thickness of about 4 monolayers. At higher concentrations the samples are a mixture of the alloy phase and metallic Sn.

For the Sn-Si system similar alloying between Sn and Si is found. At 10 vol. % Sn the bonding between Sn and Si was found to be significant, but there was still a large amount of residual Sn present in the sample. For data analysis amplitude and phase for Sn-Si pairs were calculated assuming Sn-Si to have a 50:50 atomic composition as in Sn-Ge alloy. Figure 2 compares the 10 vol. % Sn-Si RSF data to the EXAFS RSF of Sn powder and calculated Sn-Si first shell. Initial analysis finds about 49% Sn in the alloy form giving a number of near neighbors of 2.53 and a distance of 2.56 $\text{\AA}$ for Sn-Si (Sn-Sn=2.80 $\text{\AA}$, Si-Si=2.35 $\text{\AA}$) indicating that the alloying

Figure 3. RSFs for (k^3 weighted, $\Delta k = 15.61-3.1 \text{\AA}^{-1}$) Pt-SiO₂ sample (solid line) and Pt foil (dotted line).

occurs less extensively compared to Sn-Ge. In this case the larger lattice mismatch between Sn and Si seems to make the alloying less favorable.

The RSFs, for the Pt-SiO₂ sample and Pt foil are shown in Figure 3. The major peak at 2.6 Å is due to the first shell platinum neighbors. The intensity of this peak is significantly lower for the Pt-SiO₂ sample than for Pt-foil, due to small particles and increased disorder. Analysis of the filtered first shell EXAFS provides an average coordination number and bond distance of 7.1 and 2.76 Å, respectively (Table I). No evidence of Pt-SiO₂ interaction was found.

The coordination number and bond-distance obtained from EXAFS analysis were further used to calculate the size of the platinum particles⁶. On an average, the platinum particles contain about 30 atoms. The TEM measurements show that a large fraction of the platinum metal is forming small particles of diameter about 10-15 Å. Occasionally larger particles are also seen. Thus ball-milling produces highly dispersed metal particles comparable to industrial grade supported metal catalysts. While highly dispersed Pt can be produced by a variety of methods, ball milling may allow the production of highly dispersed non-equilibrium alloys difficult to produce by chemical methods.

Table I. Fitting results obtained for (a) Sn-Ge (20 vol. % Sn) and (b) Pt-SiO₂ (10 wt. % Pt) samples.

	(a) Sn-Ge pairs (T = 10 K)	(b) Pt-Pt pairs (T = 80 K)
N	2.56 ± 0.44	7.1 ± 1.0
N _{Sn-Sn}	0.36 ± 0.48	---
R (Å)	2.64 ± 0.02	2.76 ± 0.02
Δσ ² (Å ²)	0.0034 ± .0015	0.0016 ± .0002
E ₀ (eV)	-5.5	0.7

4. SUMMARY.

To summarize, we have studied the interfacial behavior of the ball milled Sn-Ge, Sn-Si, and Pt-SiO₂ systems. In each case the brittle component is found to be coated by the ductile metallic component. In Sn-Ge and Sn-Si systems, the mixing at the Sn/Ge(Si) interface causes Sn to go into the Ge(Si) structure and produce bonding consistent with cubic

SnGe and SnSi alloys. The SnGe alloy phase is found to be stable to temperatures well above the bulk Sn melting point. The results for the Pt-SiO₂ system demonstrates the capability of producing highly dispersed metals through ball milling.

ACKNOWLEDGEMENTS

This work is supported by the U.S. Department of Energy, Division of Materials Sciences, under Contract No. DE-AC02-76CH00016. The X-11 beamline is supported by the DOE Division of Materials Sciences under Contract No. DE-AS05-80-ER10742.

REFERENCES

- 1) J.K.D.S. Jayanetti, S.M. Heald, and Z. Tan: submitted to Phys. Rev. B
- 2) J.S.C. Jang and C.C. Koch: J. Mater. Res. **5** (1990) 325.
- 3) J. Mustre, Y. Yacoby, E.A. Stern and J.J. Rehr: Phys. Rev. B **42** (1990) 10483.
- 4) H. Hochst, M.A. Engelhardt and I. Hernandez-Calderon: Phys. Rev. B **40** (1989) 9703.
- 5) P. Boolchand and C.C. Koch: J. Mat. Res. (in press).
- 6) F.W.H. Kampers, C.W.R. Engelen, J.H.C. van Hooff and D.C. Koningsberger: J. Phys. Chem. **94** (1990) 8574.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**DATE
FILMED
01/10/93**