JOURNAL OF CHEMICAL EDUCATION

Laboratory Experiment

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Observing Tin−Lead Alloys by Scanning Electron Microscopy: A Physical Chemistry Experiment Investigating Macro-Level Behaviors and Micro-Level Structures

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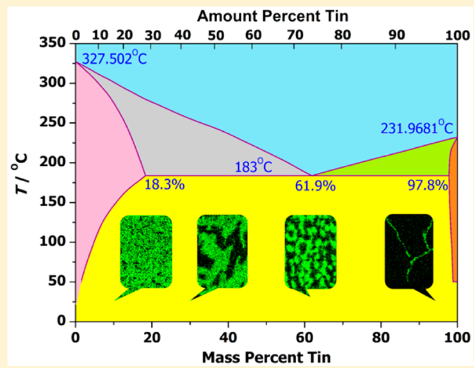
Ⓢ *Supporting Information*

ABSTRACT: Scanning electron microscopy (SEM) was introduced into undergraduate physical chemistry laboratory curriculum to help students observe the phase composition and morphology characteristics of tin−lead alloys and thus further their understanding of binary alloy phase diagrams. The students were captivated by this visual analysis method, which allowed them to more fully consider the relationship between macroscopic behaviors and microscopic structures of materials. During this process, the abilities of critical thinking were inspired, and a spirit of team work came into being.



KEYWORDS: *Second-Year Undergraduate, Physical Chemistry, Laboratory Instruction, Collaborative/Cooperative Learning, Hands-On Learning/Manipulatives, Phases/Phase Transitions/Diagrams, Instrumental Methods, Solids*

■ INTRODUCTION AND BACKGROUND

The measurement of the phase diagram for a binary tin−lead alloy system is a conventional undergraduate experiment. Thermal analysis methods are usually used to determine the phase transition temperatures, by which the liquidus and solidus lines on the phase diagram can be drawn.[1−7] Nevertheless, the diagram thus determined cannot show students directly the chemical compositions and alloy constitutions in different regions. Although the light optical microscopy (LOM) is convenient in metallography study, the chemical compositions cannot be determined by this method, and the complex patterns on the alloy surfaces are difficult to interpret by the inexperienced undergraduates. The chemical composition of the microstructural features can be determined at higher magnification by a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The incident electron beam interacts with the specimen to produce secondary electron, backscattered electron, and characteristic X-ray signals, which give the information for surface morphology, composition contrast, and elements, respectively. The characterization capabilities of EDS are mainly due to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum.[8] Thus, SEM/EDS is worth consideration as an ideal technique for analysis of the microstructure of binary alloys with varying composition.

SEM/EDS has been widely used to help the students cultivating scientific literacy and manipulative skills in the realm of nanotechnology,[9,10] dentistry,[11] archeology,[12] and geology.[13] This technique is also involved in middle school activities[14] as well as undergraduate experiment courses.[15] Although there are reports that describe the utilization of SEM and EDS instrumentation in laboratory investigations, these techniques are not yet commonplace in undergraduate material science and chemistry curricula. The experiment described in this manuscript addresses this issue; this laboratory investigation employs the use of SEM and EDS instrumentation to relate the physical properties of metal alloys to the microstructure of the materials. The notable difference of atomic number between lead and tin gives a sharp contrast between the α and β solid solutions of tin−lead alloys in SEM/EDS images. It is easy to analyze the chemical compositions in the microzones on the alloy surface, and the element distributions of various phase regions can be measured quantitatively. By SEM/EDS method, the students will observe the concrete visual evidence of phase equilibrium with solid−solid solubility. With the SEM/EDS data measured by the students, it is expected that they can describe the actual phase-transition process corresponding to the changes in the slope of the thermal analysis plots. The thermal analysis and SEM/EDS complement each other ideally,

DOI: 10.1021/ed500869d
J. Chem. Educ. XXXX, XXX, XXX−XXX

which gives the students an opportunity to develop the intuitive understanding of the crystallization process of tin−lead alloys with various compositions.

■ EXPERIMENT OVERVIEW

The SEM observation of tin−lead alloys was designed as an opening experiment during a 17-week semester and arranged 4 lab hours weekly for a research group of 4−6 students. The research groups were organized spontaneously by the students. Each group could book a time slot to measure four pieces of tin−lead alloy samples with different compositions, which were polished by the students in their spare time. The SEM images and data were uploaded to the experimental teaching web and shared by all the students. The students were required to finish their reports of tin−lead phase diagram experiment independently with both the results from thermal analysis and SEM. Students were encouraged to use web-based resources to correspond in regards to their experimental data. It was expected for students to compare outcomes for the purpose of extracting best practices for future iterations of the laboratory investigation. During each spring semester at Tongji University, about 50 students in 10 research teams participated in this opening experiment, and more than 40 alloy samples with different compositions were investigated by SEM/EDS method. Several lectures focusing on the theory and practice of SEM precede the analysis of tin−lead alloys so that the students can better understand the operation process along with the images and data obtained when they are getting involved in the microscopy measurement. (Details are in "Experiment Contents-General Information" in the Supporting Information.)

■ EXPERIMENTS

Chemicals

Tin and lead particles were purchased from Sinopharm Chemical Reagent Co., Ltd. in analytical reagent grade and used without further purification. Commercial graphite powder, epoxy resin, abrasive papers for metallograph, and abrasive grains were used.

Apparatus

High-resolution field emission scanning electron microscopy (Hitachi S-4800) with EDS (HORIBA Exam Energy) was used. The analyzable elements range was Be^{4}−U^{92}. (Instruction manuals and further information about SEM and EDS are available online.[16,17])

Procedure

Sample preparation: tin−lead alloy samples for DTA experiment could be used directly. If they were extensively oxidized, some new alloy ingots should be prepared by the conventional way of fusion such as the methods described in literature.[1,5] Thick slabs of 6×5 mm^2 were cut from the ingots using a razor blade or saw blade and embedded into epoxy resin. The surface of the slab was first wet rubbed with sandpaper and then polished in water sequentially by abrasive papers for metallograph of decreasing grain sizes (W70, W63, W50, W40, W28, W20, W14, and W10) followed by wet abrasion using fine alumina grains (size less than 1 μm). The opposite surface of the slab was simply exposed by wet rubbing with sandpaper.

SEM/EDS observation. The alloy slabs were fixed on the specimen stub with double-sided adhesive carbon tapes. The morphology of the alloys was scanned in mixed mode of SE +BSE (secondary electron + backscattered electron). The SEM analyses were carried out under the following settings: 10 or 15 kV, 10 μA, and a working distance of 15 mm. To efficiently excite the X-ray line with an electron beam, the beam energy necessary for ionization was always greater in energy than the corresponding X-ray emission line by a factor of 1.5−3. Therefore, the characteristic X-ray lines of Sn L shell and Pb M shell were detected for qualitative and quantitative analysis in EDS measurement. Details of the SEM/EDS principle and experimental procedure are included in "Experiment Contents-Students' Handout" in the Supporting Information.

■ HAZARDS

Tin is nontoxic but may be harmful if inhaled, swallowed, or adsorbed through skin or eyes. Lead is toxic and harmful if swallowed or inhaled. Lead may damage the unborn child, is suspected of damaging fertility, and can cause damage to organs through prolonged or repeated exposure. Students must wear complete suit protecting against chemicals, gloves, and safety glasses with side-shields. The alloy ingots must be prepared in a fume hood. Polishing of the slab surface must be conducted in water. Recent material safety data sheets (MSDS) should be consulted. All used chemicals and polished powders must be collected in the labeled heavy metal waste containers and be disposed of according to local regulations and procedures.

In normal operation conditions, there is no shock hazard from the EDS detector. The electron trap must be fitted to the EDS detector at all times when installed to a microscope column. For SEM, beware of electric shock, high temperature, and low temperature. Instruction manuals for SEM and EDS must be consulted before the experiment. (See "Experiment Contents-Hazard and Disposal" in the Supporting Information; instrument manuals can be found online.[16,17])

■ RESULTS AND DISCUSSION

We present here the SEM/EDS images of Sn 80% (wt) alloy shown in Figure 1. During the measuring process of SEM, the

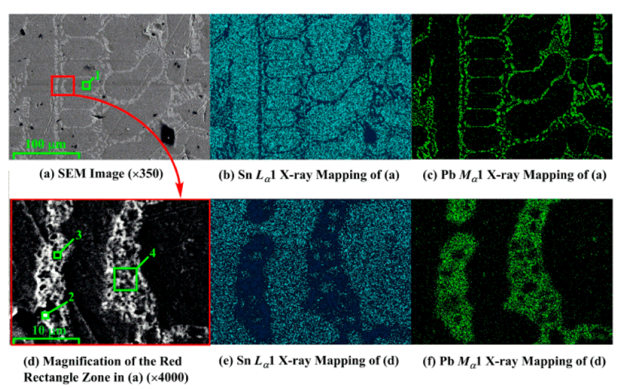


Figure 1. SEM/EDS images of Pb−Sn alloy with Sn 80% (wt).

beautiful and perplexing image (Figure 1a) made the students fascinated and puzzled since they did not expect these complicated patterns on the mirror surface of the alloy. Further investigations by EDS revealed that the darker bulks in Figure 1, panel a were rich of tin element (in Figure 1b as blue and black for Figure 1c), while the slim stripes in the gaps among the bulks in Figure 1, panel a were rich of lead element (in Figure 1c as green). The structure of the stripes was magnified (Figure 1d), and it could be observed that they were not in

DOI: 10.1021/ed500869d
J. Chem. Educ. XXXX, XXX, XXX−XXX

single homogeneous phase. The EDS results showed that the stripes consisted of lead-rich zones and tin-rich dots mingled with each other (Figure 1e,f).

The elemental analyses were carried out in four representative zones (depicted as yellow rectangle zones in Figure 1a,d). The corresponding EDS spectra are shown in Figure 2, and the

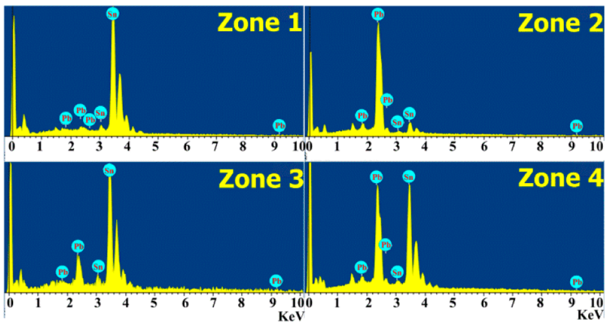


Figure 2. EDS spectra of zones 1−4 in Figure 1, panels a and d.

Table 1. Elemental Analysis of Various Zones in Figure 1, Panels a and d

	Sn *L*		Pb *M*	
zone	weight percent	atomic percent	weight percent	atomic percent
1	97.96	98.82	2.04	1.18
2	15.69	24.52	84.31	75.48
3	86.19	91.59	13.81	8.41
4	61.15	73.32	38.85	26.68

results are listed in Table 1. According to phase diagram and data for Pb−Sn system in literature,[18] the darker bulk (zone 1) corresponds to the β solid solution with the composition of Sn % (wt) above 97.8%. There are two phases in the slim stripes around the bulks, one corresponds to the α solid solution (zone 2), and the other seems like the β solid solution (zone 3, Sn 86.19% (wt), lower than 97.8% (wt) in literature[18]). The overall composition of the stripe is Sn 61.15% (wt) (zone 4), which corresponds to the eutectic composition at 61.9% (wt).

These SEM/EDS observations and analyses helped the students virsually understand the solidification process of molten Pb−Sn alloy of Sn 80% (wt). The students presumed that small bulks of β solid solutions were formed first and grew larger gradually when the system was cooled down below the liquidus temperature. The residual molten components, meanwhile, were pushed toward the gaps between the bulks. Finally, the molten residual reached the eutectic composition and solidified simultaneously to form the slim strips, with a pattern of cross-distribution of α and β solid solutions. In comparison with the phase diagram measured by thermal analysis, the students predicted that much more β solid solution would be solidified first and that much less eutectic residual remained for the alloy with Sn composition higher than 80%.

The students' presumption seems to be supported by the SEM/EDS images of Sn 95% (wt) alloy (Figure 3), in which the zones of darker bulks are enlarged, and the slim strips become thin and sparse. In their final reports, the students commented that SEM/EDS method showed a visual explanation of the level rule for phase equilibrium. Someone even discussed how to demostrate the level rule experimentally.

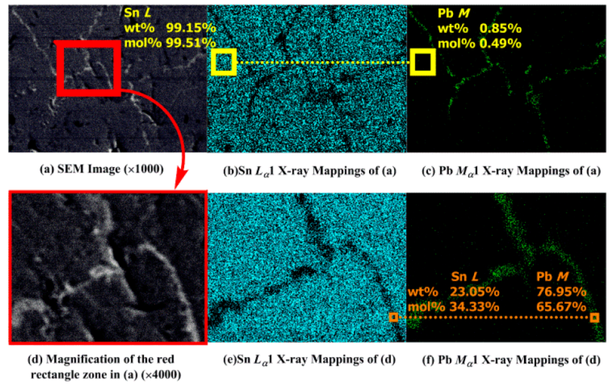


Figure 3. SEM/EDS images of Pb−Sn alloy with Sn 95% (wt).

SEM/EDS images for the other four alloys are shown in Figure 4, coupled with the phase diagram of Pb−Sn system. For

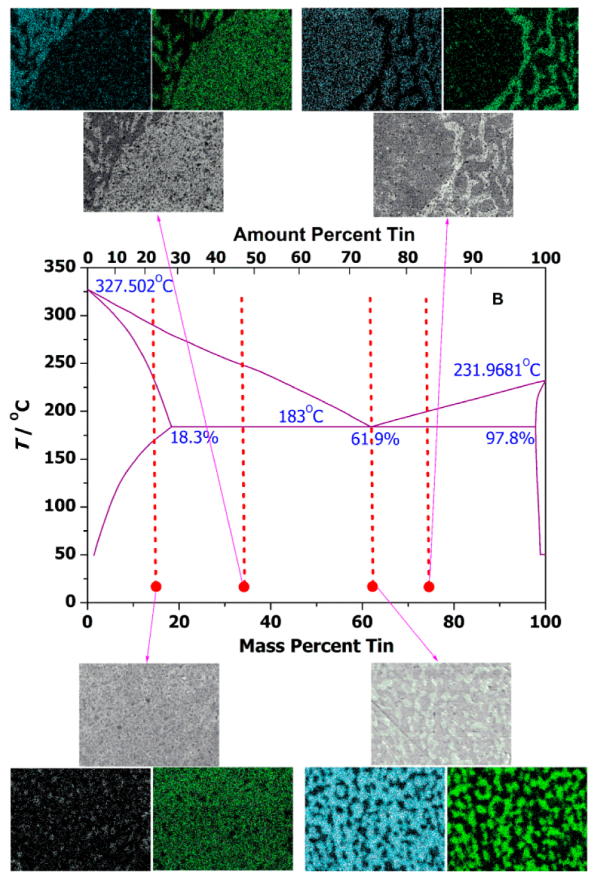


Figure 4. Phase diagram and typical SEM/EDS images of Pb−Sn alloys (×4000). Gray, SEM images; blue, Sn L_α1 X-ray mappings; green, Pb M_α1 X-ray mappings.

the alloy of Sn 35% (wt), a lamellar eutectic matrix is formed around the edge of a large bulk of α solid solution. For the alloy of Sn 75% (wt), on the contrary, a large bulk of β solid solution is found. These two sets of images show the characteristic difference of phase equilibrium components between the alloy compositions below and above the eutectic point. No large bulks are found for the alloy of Sn 62% (wt), and only the lamellar eutectic matrix can be seen. As for the alloy of Sn 15% (wt), the main phase component is the α solid solution, and only tiny amount of little tin-rich dots is weakly observed,

DOI: 10.1021/ed500869d
J. Chem. Educ. XXXX, XXX, XXX−XXX

which is due to nonequilibrium solidification during the initial cooling process.[19] More investigating results are included in "SEM-EDS Images & Data" in the Supporting Information.

Students were intrigued by the SEM and EDS analyses of the metal alloys. Students used web-based materials to confer among each other regarding their results. In the event that a sample showed an inconsistent correlation, students reviewed the methodologies used for alloy formation, namely fusion temperature, cooling rate, and heat liberated through polishing steps. The discussions created a strong connection with the experimental contents of thermal analysis and phase equilibrium. Investigation afterward showed that the students became more open-minded and active in learning. On the basis of the experience of cutting and polishing the ingots, the students tried to explore the relationship between the hardness of the Pb−Sn alloys with the chemical compositions and phase components. Further thinking and deeper understanding for phase transition/phase diagram can be seen from the students' final reports, in which above 90% of students could distinguish the structural differences among the terminal solid solution, hypoeutectic alloy, and hypereutectic alloy on the phase diagram. Before completion of SEM/EDS measurement, these phase components were only mentioned in general as mixtures of solid tin and solid lead.

■ CONCLUSIONS

This experiment is derived from a conventional physical chemistry experiment (i.e., phase diagram measurement). SEM/EDS method provides a visual correlation between microstructural characteristics of binary alloys and thermal data illustrated on phase diagrams and gives the students opportunity to explore the microscopic world. Investigating the microstructure of materials with visual methods is of great importance for the students majoring in chemistry and material science. It is beneficial to introduce modern lab techniques through a familiar topic to the students, especially of low grades, and engage the students to discover the relationship between macro behaviors and micro structures at the beginning of their academic lives.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Overview of the experiment arrangement and pedagogy; handout for students; hazards and disposal information; selected SEM/EDS images of Pb−Sn alloy samples. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to express appreciation to the students of 2012, both from the School of Material Science and Engineering and Department of Chemistry, in conducting this experiment. This work was supported by grants from the Administrative Office of Laboratory and Equipment, Tongji University (No. 1380104072, No. 1380104077).

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