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Sungil Cho, Jin Yu
Department of Materials Science and Engineering
Korea Advanced Institute of Science and Technology (KAIST)
373-1 Kusung-dong
Yusung-gu
Daejon 305-701
Korea

Sung K. Kang, Da-Yuan Shih
IBM Research Division
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598

Research Division
Almaden - Austin - Beijing - Haifa - India - T. J. Watson - Tokyo - Zurich

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Study on Oxidation of Lead-Free Sn Alloys by Electrochemical Reduction Analysis

Sungil Cho[1], Jin Yu[1], Sung K. Kang[2], and Da-Yuan Shih[2]

[1]Department of Materials Science and Engineering
Korea Advanced Institute of Science and Technology (KAIST)
373-1 Kusung-dong, Yusung-gu, Daejon 305-701, Republic of Korea

[2]IBM T. J. Watson Research Center, Yorktown Heights, NY 10598, USA

ABSTRACT

The oxidation of pure Sn and Sn-0.7Cu, Sn-3.5Ag, Sn-1Zn, and Sn-9Zn alloys at 150°C was investigated. Both the chemical nature and the amount of oxides were characterized using electrochemical reduction analysis by measuring the electrolytic reduction potential and total transferred electrical charges. X-ray photoelectron spectroscopy (XPS) was also conducted to support the results of reduction analysis. The effect of Cu, Ag and Zn addition on surface oxidation of Sn alloys is reported. For Sn, Sn-0.7Cu and Sn-3.5Ag, SnO grew first and then the mixture of SnO and SnO_2 was found. SnO_2 grew predominantly for a long-time aging. For Zn-containing Sn alloys, both ZnO and SnO_2 were formed. Zn promotes the formation of SnO_2. Sn oxide growth rate of Pb-free solder alloys was also discussed in terms of alloying elements.

Key words: oxidation, Pb-free solders, Sn alloys, electrochemical reduction analysis, Zn addition, oxide growth rate.

1. Introduction

Most metals tend to form surface oxides spontaneously under an ambient or aqueous condition.[1,2] The presence of oxides on the surface of solder alloys used in microelectronics applications is of critical importance, because it affects the formation of otherwise a good solder joint by degrading their wettability and solderability.[3,4] In manufacturing, a flux material is typically used to reduce surface oxides and to protect the joining surfaces from further oxidation during reflow at elevated temperatures. However, flux materials do not guarantee the oxide-free surfaces during soldering[5]. Especially for Pb-free solders, the oxidation behavior would be different according to various alloying elements. Therefore, the knowledge of surface oxidation could be critical for developing new flux materials.

Continued interaction of oxygen with solder during the service period of microelectronics products can also affect the mechanical reliability of solder joints. It was reported that when a Pb-rich Sn solder is fatigued in air, the intergranular cracks dominate, while fatigued in a vacuum, the transgranular cracks dominate. The fatigue life is also shortened for the air-fatigued samples, suggesting that oxygen diffusion at grain boundaries plays an important role in the lifetime of solder joints.[6] Hence, it is important to characterize the oxidation behavior of solder joints to better understand their reliability issues.

In case of Pb-Sn alloys, tin is preferentially oxidized at surface. Bird[7] and Farrell[8] have found a surface enrichment of tin in Pb-Sn alloys using X-ray photoelectron spectroscopy (XPS). Konetzki and Chang[9] found that tin was preferentially oxidized on the surface of Sn-Pb alloys containing only 2.9 at%Sn. Bevolo et al.[10] and Shah[11] showed that SnO_2 was enriched at the outer surface and the surface was completely covered with an SnO_2 layer in the laboratory environment. High-Pb alloy such as Pb-3at%Sn has been shown to exhibit surface segregation of tin in the presence of oxygen.[12] Cho et al.[13] recently reported that tin is preferentially oxidized at the surface of high Pb-Sn solders and if tin is depleted by any reason, especially below the solubility limit of tin in lead, Pb-oxides form at the surface, which might cause wetting problems. These results indicates that it is very important to know the type of oxide as well as its amount to better understand the soldering process and wetting properties of Pb-containing or Pb-free solders.

There are many techniques[1,8,10,14,15] to characterize the surface oxides. Among those, electrochemical reduction analysis is known to be an inexpensive, simple and yet relatively

precise technique to measure quantitatively both the type and thickness of oxides formed on metal surfaces[4]. In this study electrochemical reduction analysis was used to study the oxidation of Pb-free Sn alloys.

2. Experimental Procedure

Figure 1 shows a schematic diagram of the electrochemical reduction analysis. The surface to be analyzed is brought in contact with a borate buffer solution. A constant cathodic current is applied between the surface and an inert counter electrode[4]. The change of cathode potential of the oxidized surface during reduction is recorded as a function of time relative to a reference electrode. The recorded potential-time curve consists of a series of potential durations (plateaus), which is characteristic of each type of oxides reduced. Equilibrium reduction potentials of oxides can be calculated from thermodynamic stability data using Nernst equation.[13] The equilibrium and experimental reduction potentials for Sn, Pb and Cu oxides are shown in Table 1. These values were used as a standard to identify different types of oxides in the reduction curves. The width of a plateau is directly proportional to the charge density consumed for oxide reduction which indicates the amount of oxide reduced. After completing the reduction process, the final plateau of hydrogen evolution begins due to the reduction of the electrolyte. The hydrogen evolution potentials on various metals have been verified to be low enough for oxides to be completely reduced before the onset of hydrogen evolution.[13] All electrochemical experiments were performed in nitrogen-saturated pH 8.4 borate buffer solution (9.55 g/l sodium borate and 6.18 g/l boric acid)[18] which provides a minimal solubility for tin oxides using Ag/AgCl as a reference electrode (+0.2224 vs. SHE).[4,11,19]

Pure Sn and Sn alloys (Sn-0.7Cu, Sn-3.5Ag, Sn-1Zn, Sn-9Zn in weight %) were prepared by casting and rolling. The surface of test samples was fully reduced electrochemically to remove surface oxides before placed in an oxidizing furnace. Samples were thermally oxidized in a furnace at 150°C in dry air.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS or ESCA) were applied for surface analysis of oxides. Auger analysis was carried out on a PHI Model 4300 operated at 2×10^{-7} Torr. A primary electron beam energy of 5keV and 300nA was used. An argon ion gun with a voltage of 3keV and 15mA (current density = 120 μAcm^{-2}) was employed for depth profiling. XPS data were obtained using a VG Microtech, ESCA2000 which

was equipped with a Mg source (Mg Kα). The pressure in the analyzer chamber was maintained at less than 10^{-7} Torr during analysis. The Mg X-ray beam was operated at 12kV and 15mA.

3. Results and Discussion

3.1. Oxidation of pure Sn

Figure 2 shows the oxidation of pure tin foil at 150°C in dry air. The native oxide which was freshly formed on a clean surface right after reduction (i.e., as-reduced) was SnO and the thickness was about 10Å. The reduction potential of SnO in the native oxide was about –0.8 V which is close to the equilibrium value. As the aging time increases, the reduction potential of SnO tends to shift toward negative voltage. SnO grows up to 4 h and shrinks a little bit for 12 h, indicating a part of SnO transformed to SnO_2, and then SnO_2 grew for the longer oxidation time. The reduction curve of 12 h aging clearly shows two potential plateaus; the more positive one is SnO and the more negative one is SnO_2. It was difficult to make a clear distinction between SnO and SnO_2 in the reduction curves for the long-time aging. For 20 days oxidation, the reduction potential starts at about -1.1V and therefore it seems that SnO_2 exists at the outer surface region. This was indeed verified by XPS analysis as shown in Figure 3, where several XPS spectra of a pure tin foil oxidized at 150°C for different oxidation times are displayed. The spectra were analyzed using the software "XPSPEAK" to separate peaks from the spectrum of the as-reduced samples. Tin has three different chemical states, pure metal and two oxidation states, and in principle the chemical shift should differ for each state. Farrell[8] had obtained the binding energies of tin 3d from tin and its oxides using pure metal and oxide powders, as listed in Table 2. From Figure 3, it is clear that one metallic and two oxidation states of tin can be differentiated owing to the chemical shift. The binding energies of tin 3d obtained from this experiment were tabulated in Table 2, which is in good agreement with the result of Farrell[8] and Handbook[20]. The spectrum of as-reduced sample in Figure 3 shows the pure tin peak at 484.0eV. The depth resolution of XPS for metal[7] is about 20Å and therefore the detection of pure tin peak indicates that the thickness of native oxide is less than 20Å, which is in good agreement with the value (~10Å) obtained from the electrochemical reduction analysis.

3.2. Oxidation of Pb-free Sn alloys

Figure 4 shows the reduction curves from the oxidized surfaces of Sn-0.7Cu and Sn-3.5Ag foils. They exhibit almost the same behavior as the pure Sn. The native oxide consists of SnO. The mixture of SnO and SnO_2 exists after about 16 h, and SnO_2 grows predominantly for the oxidation of 3 days or longer. In view of Gibbs free energy of oxide formation as shown in Table 1, SnO_2 is expected to be more stable than SnO. However, the amount of SnO formed is almost the same for both 16 h and 3 days at 150ºC. As shown in Figure 6, both the addition of Cu and Ag into pure Sn did promote the formation of Sn oxides and the oxide growth rate of Sn-0.7Cu is higher than Sn-3.5Ag.

Figure 5 shows the oxidation behavior of Zn-containing Sn-rich solders; (a) Sn-1Zn, and (b) Sn-9Zn. Both Sn oxides and Zn oxides were formed on the oxidized Zn-containing solders. However, only Sn oxides were detected by the electrochemical reduction analysis as shown in Figure 5, while ZnO was detected by XPS analysis. It is interesting to note that for Sn-1Zn, the native oxide consists of a small amount of SnO and mostly SnO_2. Once the thermal aging starts, only SnO_2 is found. For Sn-9Zn, no SnO is found even in the native oxide, and only SnO_2 grows fast. This result indicates that Zn promotes the formation of SnO_2 and suppresses SnO, which is in good agreement with a previous result[21]. K. L. Lin et al.[21] also reported that Zn protects Sn from oxidation and therefore Zn-containing Sn alloys show a lower oxide growth rate than pure Sn and eutectic Sn-Pb. However, in this study, as shown in Figure 6, the oxidation behavior of Zn-containing Sn-rich solders displays an opposite trend. While the oxide growth rate of pure Sn is almost the same as Sn-1Zn, the oxide growth rate on Sn-9Zn is the fastest among all other alloys for the oxidation at 150ºC up to 3 days.

Summary

The electrochemical reduction analysis method has been successfully applied to investigate the oxidation behaviors of pure Sn and several Pb-free solders. XPS was also employed to supplement the results from the electrochemical analysis of oxides. Several important results are summarized as follows.

1) The electrochemical reduction analysis has detected the native oxide formed on pure Sn, Sn-0.7Cu and Sn-3.5Ag to be SnO and its thickness being about 10Å.

2) For the oxidation of pure Sn, Sn-0.7Cu and Sn-3.5Ag at $150^{o}C$, SnO was formed first on the surface and the mixture of SnO and SnO_2 was found for an extended oxidation time less than one day. For a long-time oxidation of a few days, SnO_2 grew predominantly.

3) Cu and Ag promote the formation of tin oxides in Sn-rich solders. Sn-0.7Cu shows a higher growth rate of tin oxides than Sn-3.5Ag.

4) For Zn-containing Sn-rich solders, the Zn addition promotes the formation of SnO_2 and suppresses SnO. The growth rate of SnO_2 is the highest for Sn-9Zn up to 3 day oxidation at 150ºC compared to the other alloys investigated.

Further investigation is in progress with Sn-rich, Pb-free solders with various alloying elements to correlate the oxidation behaviors with their wettability during soldering.

Acknowledgments

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Table 1. Standard Gibbs free energies[16], equilibrium reduction potentials and measured reduction potentials of Cu, Pb and Sn oxides.

Oxide	Free Energy of Formation, ΔG° (298K, kJ/mole)	Equilibrium potential (V)	Measured potential (V)
Cu_2O	-292.9[17]	-0.267	-0.625
CuO	-254.6[17]	-0.168	-0.406
PbO	-187.9	-0.4639	-0.554
SnO	-251.9	-0.7955	-0.972
SnO_2	-515.8	-0.8266	-1.10

Table 2. Binding energies of tin $3d_{5/2}$ from tin and its oxides.

Tin 3d	Farrell[8] (eV)	Experiment (eV)
Tin metal	484.2	484.0
SnO	485.9	485.9 (± 0.15)
SnO2	486.7	486.8 (± 0.23)

Fig. 1. A schematic diagram of the electrochemical reduction analysis.

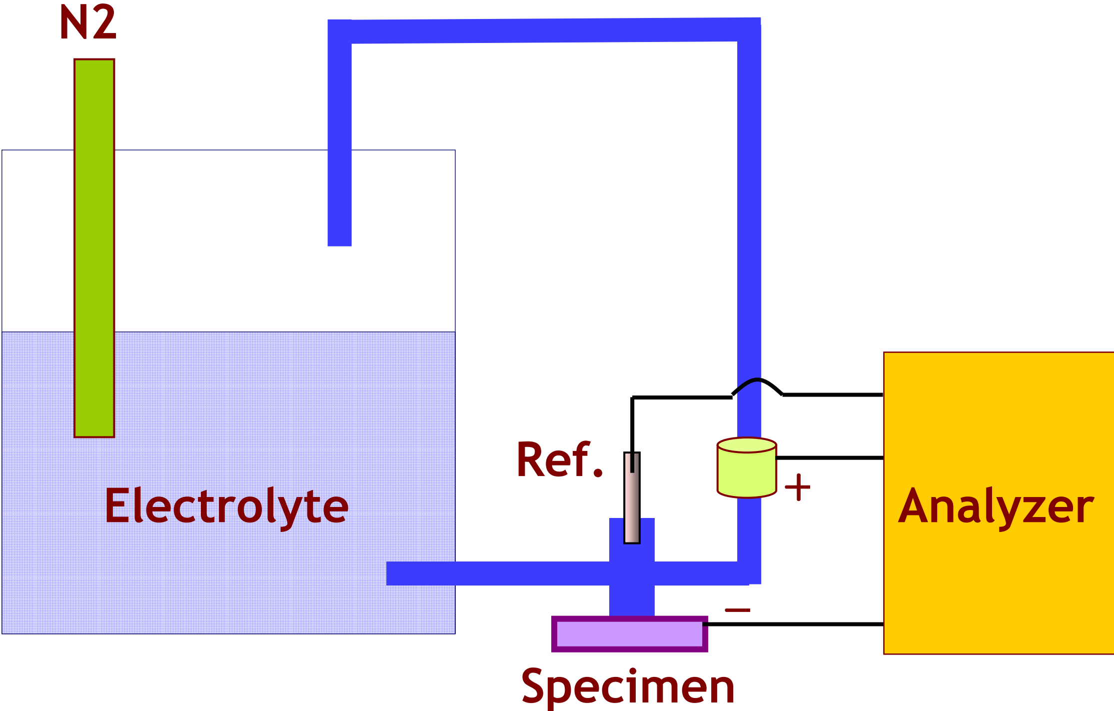


Fig. 2. Reduction curves for pure tin oxidized at 150°C in dry air.

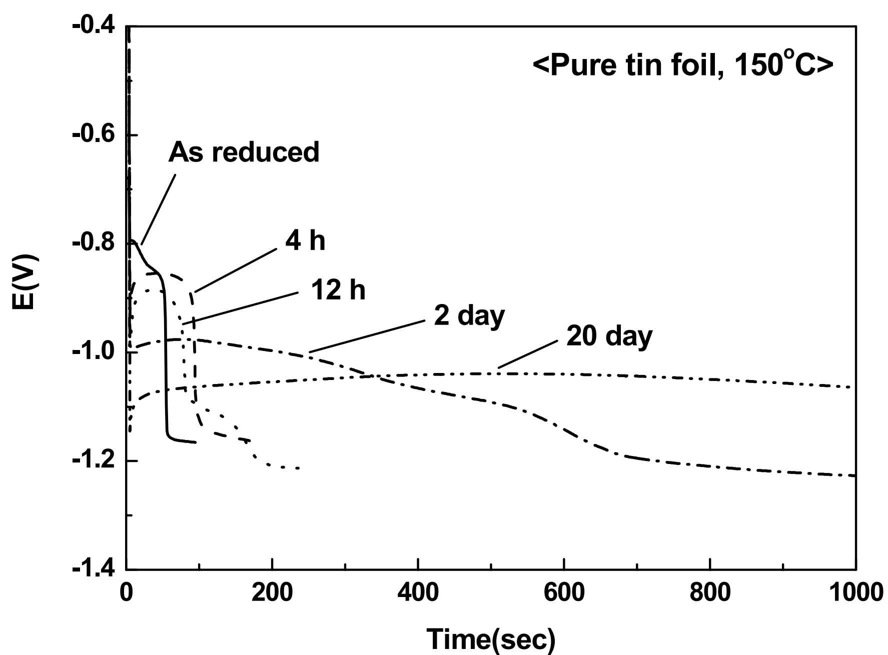


Fig. 3. XPS spectra of pure tin oxidized at 150°C for several times. The as-reduced spectrum shows a metallic Sn peak at 484.0eV.

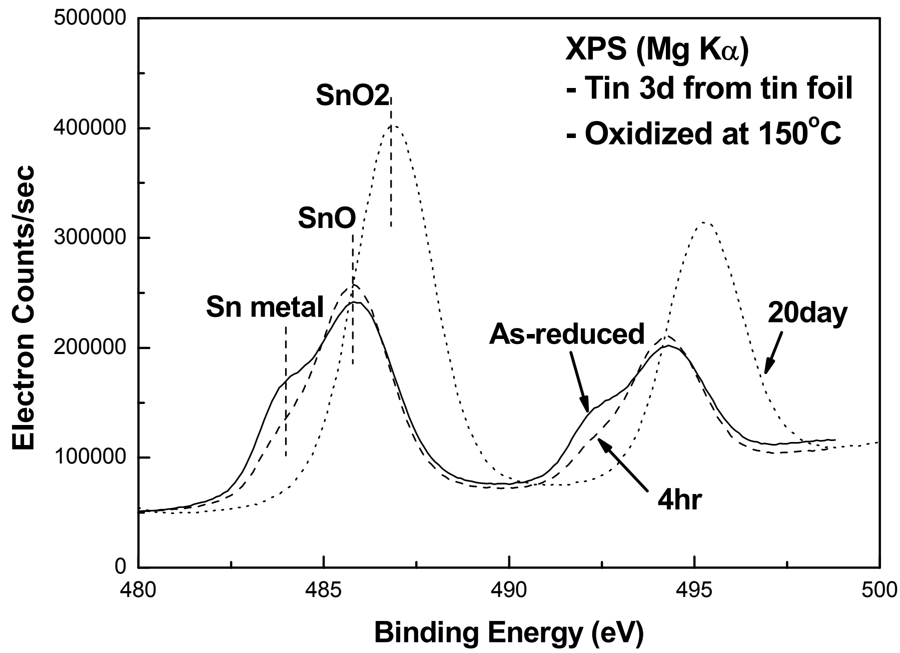
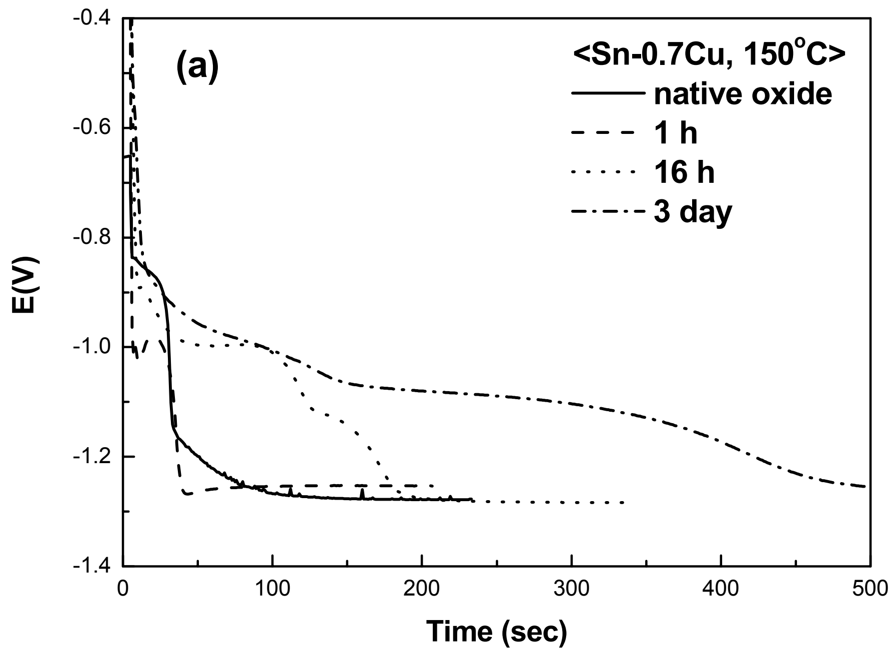


Fig. 4. Reduction curves for (a) Sn-0.7Cu and (b) Sn-3.5Ag oxidized at 150°C in dry air.



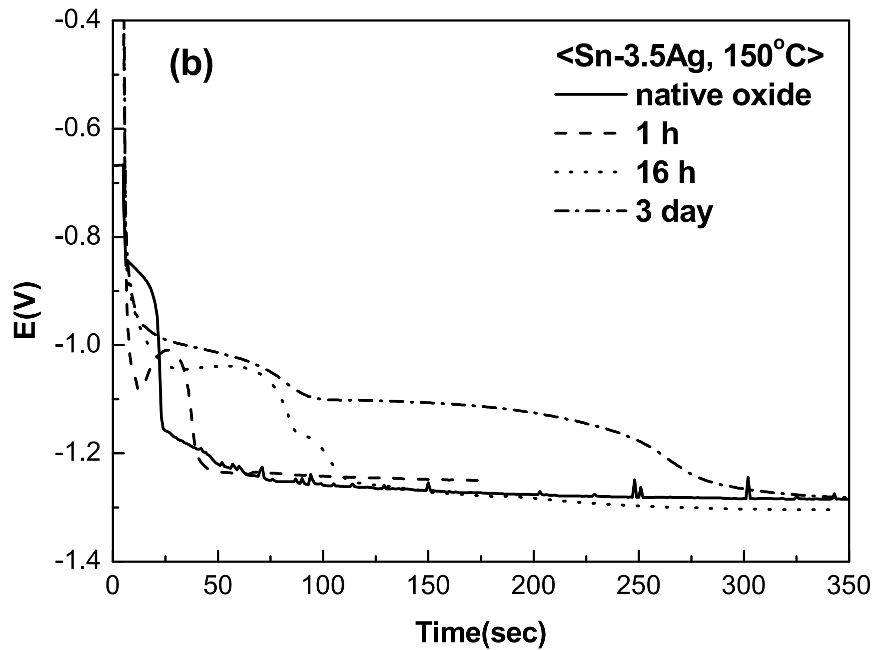
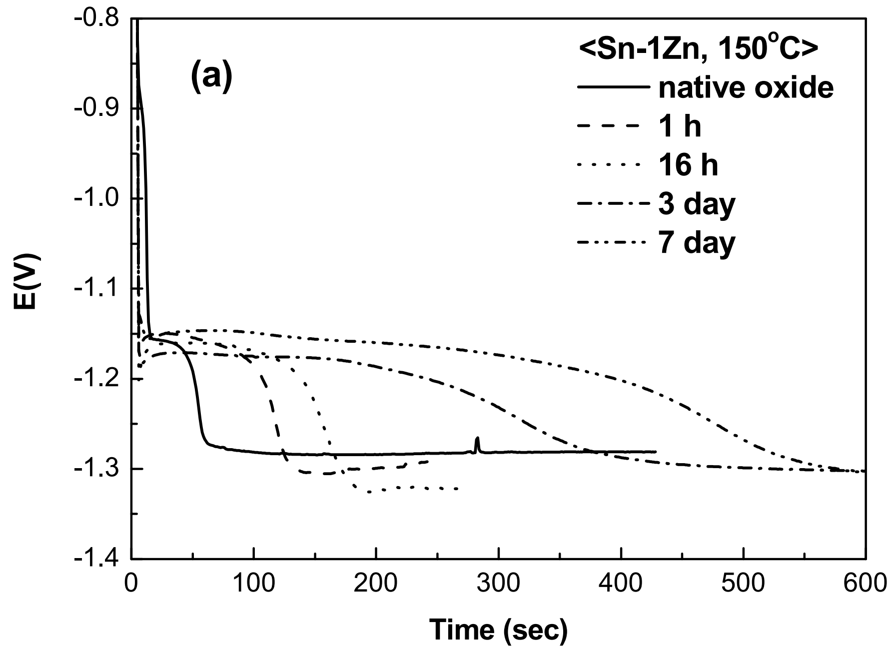


Fig. 5. Reduction curves for (a) Sn-1Zn and (b) Sn-9Zn oxidized at 150 ^{o}C in dry air.



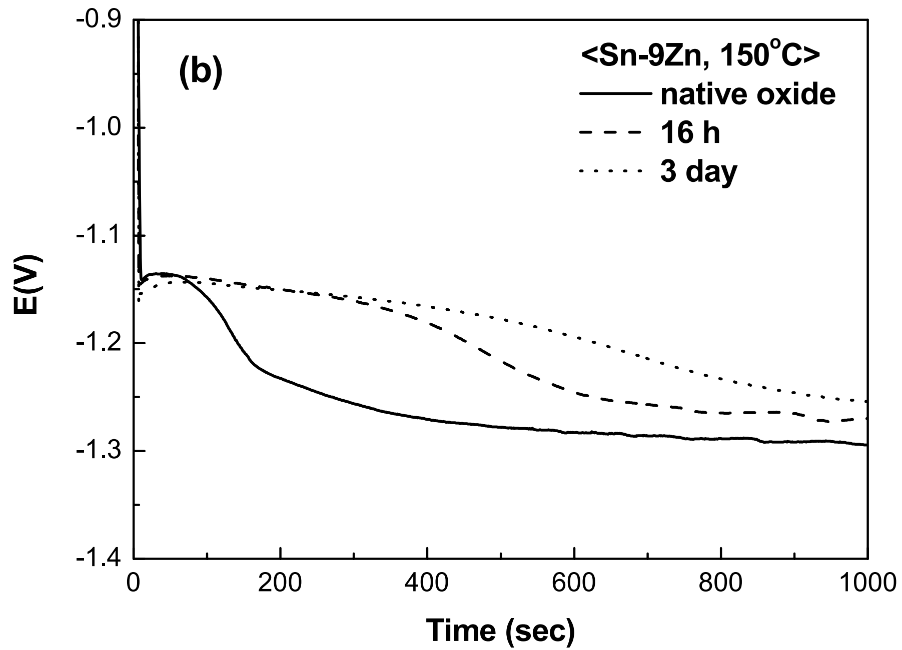


Fig. 6. Oxide growth rate of Sn and Sn alloys at 150°C in dry air.