



The kinetics and interface microstructure evolution in the internal oxidation of Ag–3at.%Sn alloy



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ABSTRACT

Based on theoretical analysis of internal oxidation kinetics, the local oxygen partial pressure within the internal oxidized Ag–3at.%Sn alloy was derived as a function of the ambient oxidation parameters firstly. Further combined with the interface structure stability diagram, the evolution of Ag/SnO₂ interface structures in internal oxidization of Ag–3at.%Sn alloy has been quantitatively clarified. The prediction results indicates that the stoichiometric Ag/SnO₂ interface dominates in internal oxidation of Ag–3at.%Sn alloy in air atmosphere at 973 K, while a gradient structures with both O-rich and stoichiometric interface were formed at the condition of 3 atm pure oxygen atmosphere at 873 K.

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1. Introduction

The internal oxidation of silver-based dilute alloy is a diffusion-controlled process in which the oxygen diffusion into the alloy and form oxides with the less noble alloying elements [1]. Because of the successfully in-situ precipitation of dispersed oxide particles in metal matrix, internal oxidation process has been applied widely to the production of oxide dispersion strengthened materials or electrical contact materials, such as Ag–SnO₂ [2], Ag–CdO [3], and Ag–ZnO [4]. The dispersed structure of oxide particles precipitated in a silver matrix highly depends on the internal oxidation conditions, which may have very significant effects on the properties of the silver substrate.

In order to understand the microstructure evolution of oxide particles precipitation behavior, there are numerous literatures have been involved into the study of internal oxidation of silver based alloys. Douglass et al. have investigated the internal-oxide-band formation during oxidation of Ag–Mg alloys [5], and the oxygen rich cluster with size of ~5 nm was found in the precipitates free zone. Charrin et al. have studied the precipitation behavior of oxide particles in internal oxidation of Ag–Mg alloys, and the formation of both stoichiometric and non-stoichiometric oxide clusters were verified [6,7]. In addition,

the evolution from hypo- to hyper-stoichiometric oxide clusters depends on the oxidation kinetics was characterized by in-situ X-ray measurements [8]. Kosec et al. have investigated the internal oxidation of Ag–Te alloy in 1 atm pure oxygen at 1023–1103 K, and two types of oxides particles were characterized [9]. Roth et al. have studied the oxidation products composition and the internal oxidation kinetics of Ag–Se alloy, and found that the appearance of second intermetallic phase may accelerate the internal oxidation process by the prior formation of the internal liquid double oxide phase [10,11]. Sato suggested that the size of precipitated oxide particles decreases with the decreasing of solute concentration and the increasing of oxygen pressure [12]. It is acknowledged that the size and distribution of oxide particles within internal oxidized region were dominated by the competition between nucleation and growth behavior of the particles at the internal oxidation front [13]. In generally, the nucleation behavior dominates initially near the surface, and numerous particles exist, whereas growth dominates in internal region, the number of particles per unit volume decreases but their size increases [14]. There are also many efforts have been focused on the internal oxidation kinetics of different silver-based alloys, which aimed at exploring the specific diffusion kinetics behavior of different materials, and further to improve the dispersed structures of oxide precipitates by optimization of internal oxidation parameters [15–17]. And also, some new in-situ measurement methods for the monitoring of internal oxidation kinetics were developed [18,19]. Although the precipitation behavior of oxide particles in internal oxidized alloys has been discussed extensively, the kinetic relationship between the microstructure

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evolution of in-situ formed oxides and internal oxidation parameters is still hard to be established and the microstructure evolution is difficult to predict in quantitatively.

In this paper, we attempt to propose a research strategy for the prediction of interface-level microstructures evolution in the internal oxidation of Ag–3at.%Sn alloy. Based on the theoretical analysis of internal oxidation diffusion kinetics, a functional relationship between the local oxygen partial pressure inside the internal oxidized region and the ambient internal oxidation parameters was derived firstly. Further combined with the interfacial thermodynamic stability diagram and properties assessment of Ag/SnO₂ interface in our previous work [20], a quantitative correlation between oxidation kinetics, internal oxidized interface microstructures as well as its properties was constructed. Finally, the prediction of Ag/SnO₂ interface structures and interfacial properties have been implemented exemplarily for the internal oxidation of Ag–3at.%Sn alloy in air atmosphere at 973 K, and pure oxygen atmosphere (3 atm) at 873 K.

2. Experimental procedure

For the investigation of internal oxidation kinetics, a series of internal oxidation experiments were implemented on different oxidation conditions. The material preparation details are as follows. An Ag–3at.%Sn binary alloy was arc melted in argon atmosphere. The as-cast alloy was then annealed in a sealed quartz tube with argon atmosphere for 50 h at 1023 K for homogenization, rolled into ~1.5 mm thick plates, and cut into 10 × 10 mm square pieces. The details of internal oxidation parameters were presented in Table 1. Internal oxidation was performed in a muffle furnace in air atmosphere or a pressurized furnace with 3 atm pure oxygen pressure. After internal oxidation, the oxidation depth of each sample was measured and the macrostructure of the internal oxidized region was characterized by using an optical microscope (MeF3A).

3. Theoretical analysis of internal oxidation kinetics

Kinetically, the internal oxidation process of Ag–3at.%Sn alloy is dominated by atomic diffusion behavior of both the solute Sn and the dissolved O in Ag. For the illustration of internal oxidation kinetics, there are various models have been developed in last decades [21–28]. More than fifty years after its publication, Wagner's model [21,22] still remains as the cornerstone of our understanding and is still the starting point for virtually every study in internal oxidation. Several hypotheses have been made in the Wagner's model, which included consideration of binary alloys only, presence of a single oxidant, oxidation of the sole most reactive metal, and formation of a single oxide with a very low solubility product. As confirmed by numerous of literatures [2,17,20], the internal oxidation behavior of Ag–3at.%Sn alloy reflects a strong match of these hypotheses in the Wagner's model.

The diffusion kinetics behavior of internal oxidation of Ag–3at.%Sn alloy was illustrated in Fig. 1, based on the Wagner's model. During the internal oxidation of Ag–3at.%Sn alloy, two

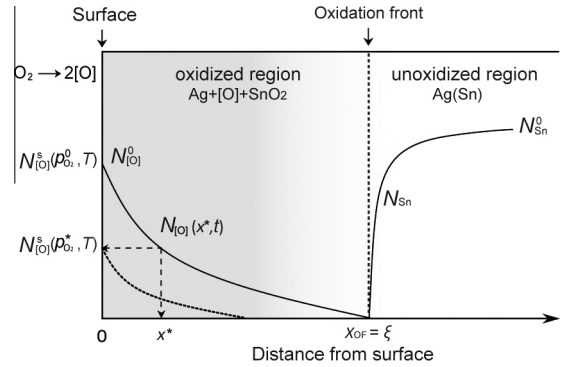


Fig. 1. Schematic concentration profiles in Ag–Sn alloy during the internal oxidation process described by the Wagner's model.

regions can be divided into the Ag matrix, the oxidized region and the unoxidized region, as seen from Fig. 1. The internal oxidation depth (ξ), which measured from the sample surface to internal oxidation front (X_{OF}), is following the parabolic rate law,

$$\xi^2 = (4\gamma^2 D_{[O]})t \tag{1}$$

where $D_{[O]}$ is the diffusion coefficient of dissolved oxygen in Ag, t is the internal oxidation time, and γ is a dimensionless parameter dependent on the relative contribution of the diffusion of the component being internally oxidized into the internal oxidation zone [29]. The parameter γ is obtained by equating the fluxes of oxygen and the internally oxidizing element at the oxidation front, which can be expressed as a transcendental function as shown in Eq. (5) below, and it can be obtained from a graphical or numerical solution. The parabolic rate constant of $4\gamma^2 D_{[O]}$ reflects the internal oxidation rate of Ag–Sn alloy.

Based on the second Fick's diffusion theory, the concentration profile of dissolved oxygen in the oxidation region ($x \leq \xi$) and that of solute Sn in the unoxidized region ($x > \xi$) can be derived separately as [30]

$$N_{[O]}(x, t) = N_{[O]}^s \left\{ 1 - \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{D_{[O]}t}}\right)}{\operatorname{erf}\gamma} \right\} \tag{2}$$

$$N_{Sn}(x, t) = N_{[O]}^0 \left\{ 1 - \frac{\operatorname{erfc}\left(\frac{x}{2\sqrt{D_{Sn}t}}\right)}{\operatorname{erfc}(\theta^{1/2}\gamma)} \right\} \tag{3}$$

where $N_{[O]}$ and N_{Sn} are the mole fraction of oxygen and Sn solute. $N_{[O]}^s$ is the equilibrium solubility of dissolved oxygen in Ag which equals to the maximum oxygen concentration at the surface, i.e. $N_{[O]}^s = N_{[O]}(0, t)$. N_{Sn}^0 is the initial solute concentration of Sn in Ag. $D_{[O]}$ and D_{Sn} are the diffusion coefficients of oxygen and Sn in Ag, respectively. $\theta = D_{[O]}/D_{Sn}$. The derivation of Eqs. (2), (3) assumes that the atomic concentration of Sn at $x = \xi$ is negligible.

At the internal oxidation front ($x = \xi$), the inwards flux of dissolved oxygen atoms must be proportional to the outwards flux of Sn atoms arriving from the inside alloy

$$\lim_{\epsilon \rightarrow 0} \left[-D_{[O]} \left(\frac{\partial N_{[O]}}{\partial x} \right)_{x=\xi-\epsilon} = n D_{Sn} \left(\frac{\partial N_{Sn}}{\partial x} \right)_{x=\xi+\epsilon} \right] \tag{4}$$

where n equals the atomic O/Sn ratio of the formed SnO₂ particles.

Using Eqs. (2)–(4), one can obtain

$$\frac{N_{[O]}^s}{n N_{Sn}^0} = \frac{\exp(\gamma^2) \operatorname{erf}\gamma}{\theta^{1/2} \exp(\gamma^2 \theta) \operatorname{erfc}(\gamma \theta^{1/2})} \tag{5}$$

Table 1
Internal oxidation parameters of Ag–3at.%Sn alloys.

Oxygen partial pressure (atm)	Temperature (K)	Oxidation time (h)
0.21 (air atmosphere)	873	0–72
	973	
	1023	
	1073	
3 (pure oxygen)	873	0–12
	973	
	1023	

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