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Letter to the Editor

Segregation anisotropy of Sn on different crystallographic orientation surfaces of coarse-grained Zircaloy-4

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) technique was utilized to study the correlation between the tendency of Sn surface segregation and the crystallographic orientation of grain surface in coarse-grained (0.2–0.8 mm in diameter) Zircaloy-4 specimen. The results indicated that the intensity of Sn surface segregation was in an order of (0001) < $(\bar{1}2\bar{1}0)$ ≈ $(01\bar{1}0)$, and it was in agreement with the prediction from bond-breaking theory.

1. Introduction

Generally speaking, many kind of alloying element atoms can segregate on alloy specimen surfaces to lower the surface free energy during heat treatment. Up to now, a lot of studies about the phenomena concerning surface segregation have been reported [1–10].

In addition, the phenomenon of surface segregation anisotropy of alloying element atoms in different alloy specimens also has been investigated. Such as, Johnson et al. [11] used the scanning auger microprobe (SAM) to study the surface segregation anisotropy of Au atoms on the surfaces of 20 grains with different crystallographic orientations at 973 K in a dilute Ni–Au alloy. Wandelt and Brundle [12] investigated the surface segregations of Cu on (1 1 1) and (1 0 0) surfaces in a Ni–Cu alloy by experimental method and theoretical prediction. Steigerwald et al. [13] reported the composition measurements on the surfaces of 38 grains with different crystallographic orientations at four different temperatures in range of 1083–1173 K in a Ni–Au alloy. Zhou et al. [14] also investigated the surface compositions of 9 different orientation grains in a Fe–Si–Sn–C alloy. All of these results obviously showed that the surface segregation of alloying element atoms were anisotropy, namely, the tendency of surface segregation of alloying element atoms depend on the crystallographic orientation of the grain surface. And all of these articles were published in 1970s–80s. Here, this topic is brought up again due to the following reasons: first, the surface segregation could affect many kinds of surface properties such as corrosion resistance, catalytic behavior and so on [1,15]. Second, the corrosion resistance of Zircaloy-4 which is widely used in pressurized water reactors (PWRs) as fuel cladding materials performs as anisotropy in the experimental results obtained by autoclave corrosion tests [16–19]. So we consider that the corrosion resistance anisotropy of Zircaloy-4 maybe arise from the surface segregation anisotropy of alloying element atoms. On the other hand, there was seldom study focusing on the surface segregation anisotropy of alloying element atoms on the surface of a HCP alloy.

In this work, we mainly focus on the correlation between the crystallographic orientation of grain surface and surface segregation anisotropy of Sn in Zircaloy-4 which is a HCP alloy. XPS technique which is one of the methods for determining surface chemical composition [20–24] was used to determine the concentrations of Sn on the grain surfaces with different crystallographic orientations in coarse-grained Zircaloy-4 specimen at an elevated temperature. Then, bond-breaking theory was used to predict the difference of Sn surface segregation intensities among different crystallographic orientation grain surfaces.

2. Experimental

In order to minimize the effect of grain boundaries on the surface segregation of alloying element atoms and rigorously observe the correlation between surface segregation anisotropy and crystallographic orientation of grain surface, a coarse-grained specimen should be adopted. Commercial Zircaloy-4 (Zr-1 at.% Sn–0.23 at.% Fe–0.16 at.% Cr) was used, and the procedures of the coarse-grained (0.2–0.8 mm in diameter) specimen preparation in detail was the same as that described in previous work [17,25,26].

The orientations of grains were determined by electron backscattered diffraction (EBSD) technique. Before EBSD tests, one piece of the specimen with 10 mm × 8 mm × 0.6 mm in dimension was electro-polished in a solution of 20 vol.% $HClO_4$ and 80 vol.% C_2H_5OH at about 273 K with 29 V DC. The grain orientations within a region of 6 mm × 6 mm in area were measured by EBSD equipped on an Apollo 300 SEM and the scanning step length was 15 μm.

XPS technique was employed with a monochromatic Al Kα source under a pressure of 7×10^{-9} mba to measure the concentrations of alloying elements on the surfaces of different grains. 5 grains with different orientations were chosen to determine. It is feasible to accurately locate the positions of these grains since the different morphologies recorded by CCD camera due to the different orientations of the different grains during the experimental process in XPS (Escalab 250 xi) equipment. Before the acquirement

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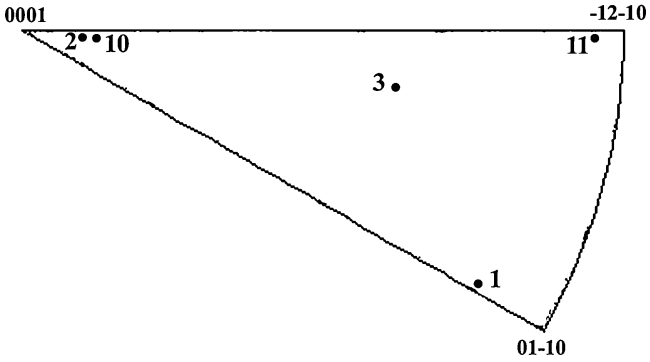

Fig. 1. Orientations of surface normal direction of 5 selected grains.

of XPS spectrum, the surfaces were sputtered by 2000 eV Ar^+ for 100 s to remove the contaminations on the surface at 298 K. After cleaning, no peak of residual C was found in XPS spectra. The survey scans of XPS spectrum acquired from surface with a binding energy range of 0–1486.6 eV and the detail spectra of Zr 3d, Fe 2p, Cr 2p and Sn 3d were acquired with a step size of 0.05 eV at 298 K. Then the specimen was heated to 873 K and kept for 15 and 60 min, respectively. Then the power supply for heating was switched off and the spectra of Sn 3d, Zr 3d on the surfaces of the selected 5 grains were acquired by XPS technique one by one after the specimen was cooled to below 313 K. About 2 min was required for the temperature of the sample to drop from 873 to 473 K. So the surface segregations of alloying elements could be maintained within 2 min during cooling. The spot size of X-ray beam was 200 μm to ensure all of spectra acquired from one grain surface. Finally, Avantage software (version 5.934) was used to deal with the XPS spectra and to calculate the atomic concentrations of alloying elements on the surfaces of these grains. But the curve fitting of the peak was not necessary in our work since we only focus on the atomic concentrations of alloying elements rather than the chemical states of alloying elements.

3. Results and discussion

The orientation of the surface normal direction (ND) for these grains used for XPS determination is plotted in an inverse pole figure (IPF) as shown in Fig. 1. The selected grains were signified as 1, 2, 3, 10 and 11. It is obvious that the orientations of grain 2 and10 are close to [0 0 0 1], the orientation of grain 1 is close to [01$\bar{1}$0], the orientation of grain 11 is close to [$\bar{1}$2$\bar{1}$0] and the orientation of grain 3 is in the middle part of the IPF.

Fig. 2 shows the detail XPS spectra of Zr 3d and Sn 3d acquired on the surfaces of these 5 grains at 298 K and after heating to 873 K for holding 15 and 60 min. At 298 K, as shown in Fig. 2a, the Sn 3d peaks (484.8 eV for Sn $3d_{5/2}$ and 493.0 eV for Sn $3d_{3/2}$) are not conspicuous, and the shift of Zr 3d peaks (178.9 eV for Zr $3d_{5/2}$ and 181.3 eV for Zr $3d_{3/2}$) is attributed to the formation of Zr_xO_y on the surface since a nanometer thickness of oxide layer formed on the surface for many metals at room temperature [27]. But the Sn 3d peaks of the spectra detected after heating to 873 K for holding 15 (Fig. 2b) and 60 min (Fig. 2c) are slightly obvious than that as shown in Fig. 2a. It means that the Sn could segregate on the surface of the specimen at elevated temperature, and the spectra of Zr 3d and Sn 3d acquired on these grain surfaces after heating to 873 K for holding 15 min are nearly the same to that acquired after heating to 873 K for holding 60 min, it shows that the chemical compositions

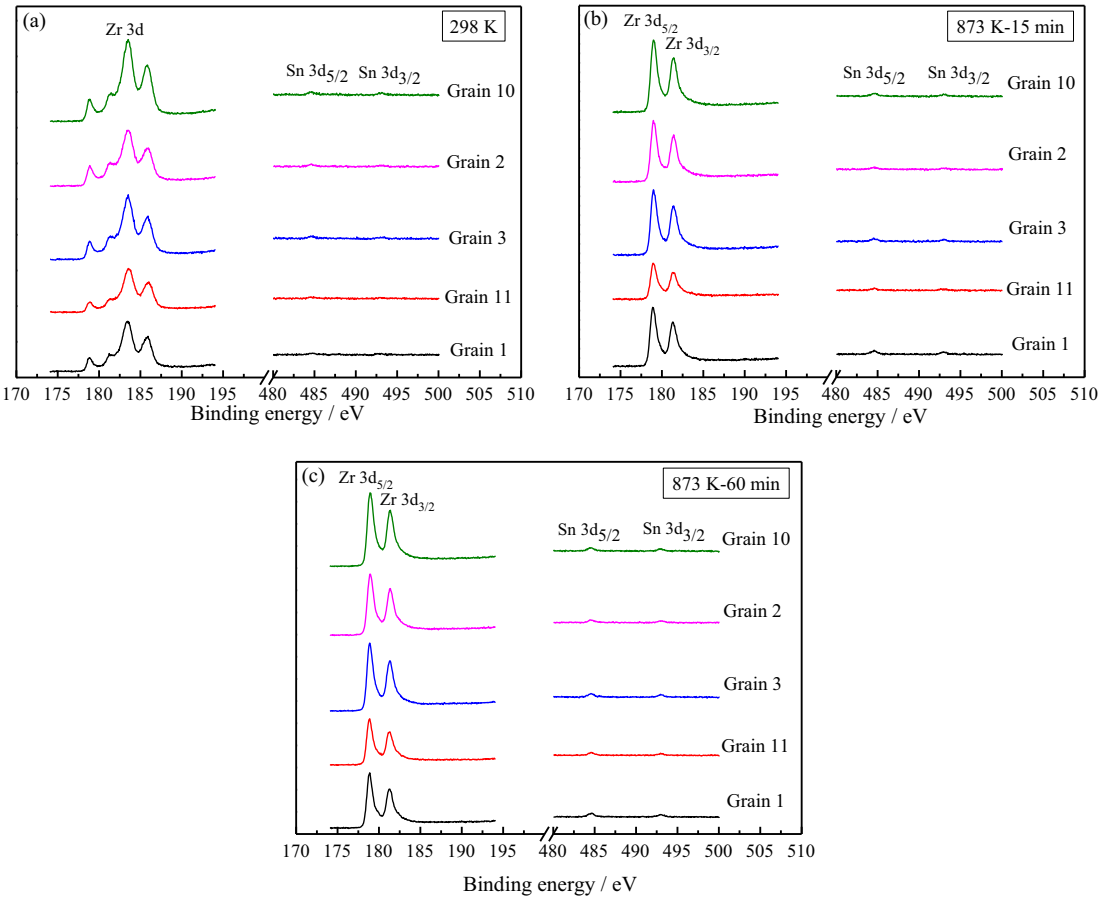

Fig. 2. The XPS spectra of Zr 3d and Sn 3d acquired on the surfaces of 5 grains at 298 K (a) and after heating to 873 K for holding 15 min (b) and 60 min (c).