Title	Local Appearance of Sn Liquid Phase at Surface of Aluminum Alloy Powder during Heating
Author(s)	Kondoh, Katsuyoshi; Luagnvaranaunt, Tachai; Threrujirapapong, Thotsaphon et al.
Citation	Transactions of JWRI. 2007, 36(2), p. 29-32
Version Type	VoR
URL	https://doi.org/10.18910/3503
rights	
Note	

Local Appearance of Sn Liquid Phase at Surface of Aluminum Alloy Powder during Heating[†]

KONDOH Katsuyoshi*, LUAGNVARANAUNT Tachai**,
THRERUJIRAPAPONG Thotsaphon** and KIMURA Atsushi***

Abstract

Local appearance of Tin (Sn) liquid phase at the surface of rapidly solidified aluminum alloy particles including Mg and Sn was investigated by X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). Sn3d photoelectron spectrum intensity gradually increased with increasing the Mg content of raw particles during heating up to 825K. AES analysis indicated that supersaturated Sn atoms by rapid solidification diffused to the particle surface in a liquid state at elevated temperature over 505K, and finally concentrated at the inner region of about 50~60 nm in depth from the topmost surface. Mg was, however, necessary for this phenomenon, because it was effective for the chemical breakage of aluminum oxide films at the particle surface by the deoxidization reaction from 670K to 700K.

KEY WORDS: (Tin) (Surface Oxide Films) (Aluminum Powder) (Deoxidization) (XPS) (AES)

1. Introduction

Solid-state sintering of aluminum alloy powder is generally difficult because aluminum oxide films of 1~2 nm thickness exist stably on the powder surface and form "barriers" to obstruct the metallurgical bonding between particles. Hot extrusion or forging with severe plastic deformation is often employed to consolidate raw aluminum powder by the mechanical breakage of surface oxide films. Some previous studies suggest the chemical resolution of oxide films by the deoxidization of magnesium (Mg), because the free energy of oxide formation in an atmosphere of Mg is smaller than that of Al at elevated temperature [1]. The experimental approach indicated that solid-state sintering completely occurred when employing Al-Mg alloy particles, and sintered materials revealed a high elongation with no fractured surface at primary particle boundaries after tensile tests. X-ray Photoelectron Spectroscopy using Synchrotron Radiation (SR-XPS) analysis [2] was applied to detect the above reaction behavior inside the very thin surface films of Al-Fe-Ni-Mg alloy powder. It was shown that only oxide state Al elements were detected in the films at less than 673K, however Al in the metallic state also appeared over 673K [3]. Furthermore, the density of the valence band increased due to the formation of high electricity materials. By using this process for the chemical breakage of aluminum oxide films, in-situ formation of

aluminum nitride (AlN) was established via the reaction between metallic aluminum element and nitrogen atoms in the heating atmosphere [4]. In the above deoxidization of surface oxide films of aluminum alloy powder and formation of AlN, additive elements such as Si, Fe and Ni do not contribute to them. Sn, however, has different properties from these additives; its solid solution in the aluminum matrix is limited, and it exists in a liquid phase over 673K, where the deoxidization of aluminum oxide surface films by Mg occurs.

In this study, the behavior of Sn at the topmost surface of the aluminum alloy powder particle at elevated temperature is investigated by XPS and AES analysis. In particular, the local appearance mechanism of Sn in a liquid phase is discussed by considering the chemical breakage of surface oxide films via deoxidization reaction by Mg.

2. Experimental

Rapidly solidified aluminum alloy powder by air-atomization, having a mean particle sizes of about 45 μm, was used as starting raw materials in this study. Table 1 shows the chemical compositions of raw powders. The supersaturated Sn content of each raw particle is 1mass%, however, the Mg content is different for each; 0, 0.5, and 1mass%. The previous study suggests that it is possible to investigate the behavior of each element at the

---

topmost surface of powder during heating by measuring the dependence of the changes in both the chemical bonding states and the intensities of their photoelectron spectra on the applied temperature by using XPS [4].

Table 1 Chemical compositions of atomized aluminum alloy powder used as input materials (mass%).

	Fe	Ni	Sn	Mg	Mn	Al
A	4.05	3.92	1.10	<0.01	Trace	Bal.
B	3.96	3.97	1.10	0.51	Trace	Bal.
C	4.07	4.03	1.07	1.02	Trace	Bal.

Al2p, Mg2p, Sn3d, and O2s photoelectron spectra are measured when each particle is heated to 825K in the chamber at a pressure below 1×10^{-7} Pa. The step-wise heating patterns at 600K for 3.6ks in the early stage, 670K for 7.2ks and 825K for 6ks in the final stage are continuously applied in this study. AES analysis is also carried out to examine the distribution of each element at the inner region below the topmost surface of the powder particles before and after heating at a sputtering ratio of 20 nm/min.

3. Results and Discussion

Figure 1 shows the changes in each photoelectron spectrum of the raw powder particles during heating to 825K. (a), (b), and (c) correspond to the Mg content of 0mass%, 0.5mass%, and 1mass%, respectively. The intensity of the Mg2p photoelectron spectrum at 50eV increases gradually according to the increase of Mg content. Significant changes in the Al2p and Sn3d photoelectron spectra are also observed. For the purpose of the detailed investigation, the changes of each spectrum at the low binding energy (40～90eV) and high range (470～550eV) are illustrated separately in **Fig.2** and **Fig.3**, respectively.
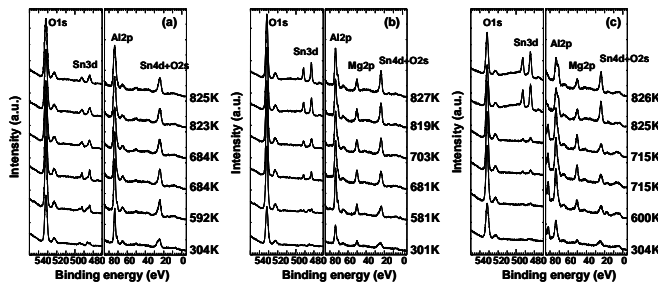

Fig.1 Changes in XSP photoelectron spectra of aluminum alloy powder with different Mg content during heating to 825K. Mg content; 0% (a), 0.5% (b) and 1% (c).

Figure 2 (a) indicates that there is no change in the aluminum spectrum, and only the oxide state (Al[O]) is observed when heating raw powder containing no Mg. On the other hand, when employing aluminum powder with Mg, both spectra of the oxide state and the metallic state (Al[M]) are detected as shown in Fig.2 (b) and (c). They also show a remarkable increase of Al[M] intensity

with increase in the Mg content of raw powder. This result suggests the chemical breakage of aluminum oxide surface films via their deoxidization reaction by Mg [5].
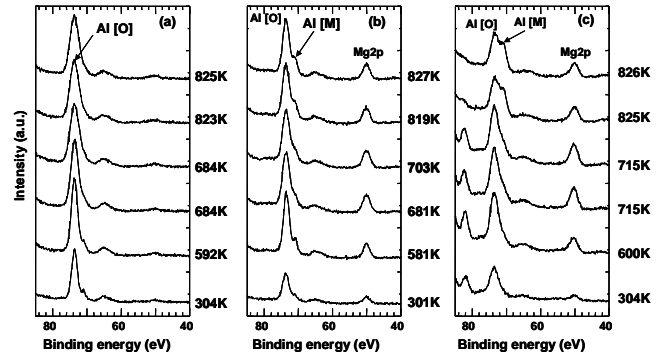

Fig.2 Effect of Mg content of raw powder on Al2p (Al[M] and Al[O]) photoelectron spectra during heating to 825K.

Figure 3 shows changes in O1s and Sn3d photoelectron spectra during heating at the high binding energy. The increase of the intensity of the Sn spectrum is detected in each raw powder during heating to 825K. This phenomenon is independent of the Mg content of the raw particles. However, with regard to Sn3d spectrum intensity at 825K, this becomes higher by increasing the Mg content. In particular, the intensities of Sn3d suddenly increase at the elevated temperature over about 700K when the raw powder particles contain Mg as shown in (b) and (c). Compared to the above results, the appearance of Sn3d spectrum is related with that of Al[M] spectrum, and is affected by the Mg content of the input powder.
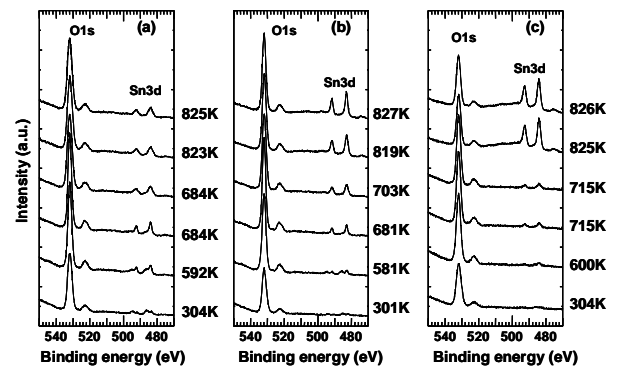

Fig.3 Changes in Sn3d photoelectron spectra related to Sn liquid phase of raw powder during

Figure 4 shows the changes in the intensities of each photoelectron spectrum, Al2p spectrum ratio α, and the temperature of the raw powder particles, where α is the intensity ratio between Al[M] and Al[O] of Al2p photoelectron spectrum. (a), (b), and (c) correspond to the Mg contents of 0, 0.5 and 1mass%, respectively. The raw powder particles without Mg show no change in the Sn3d photoelectron spectrum, on the other hand, the intensity of its spectrum increases according to the increase of Mg content. In particular, the temperature with a rapid

increase of Sn3d spectrum intensity coincides with that of changes in the Al2p spectrum ratio α, and this corresponds to XPS profiles in Fig.2 and Fig.3 as mentioned above.
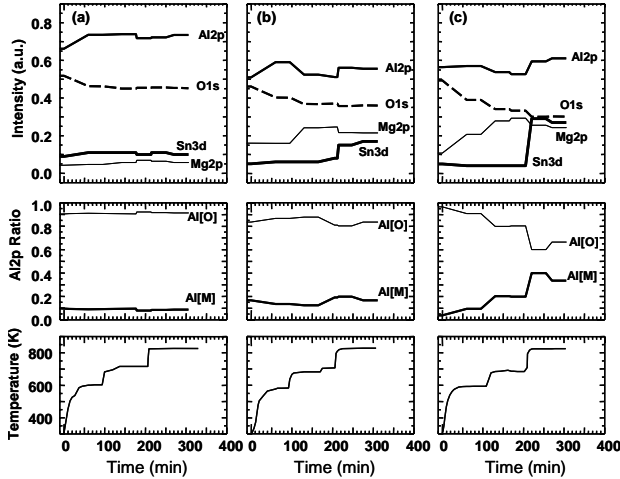

Fig.4 Dependence of each spectrum intensity and Al2p spectrum ratio on temperature of raw powder in XPS analysis. Mg content; 0% (a), 0.5% (b) and 1% (c).

For a discussion of the concentration of Sn below the topmost surface of the particle during heating, the relationship between the temperature in deoxidizing the Al_2O_3 surface films and the increase of Sn3d spectrum intensity must be investigated. The effect of Mg on the appearance of Sn in a liquid state to the powder surface will be also considered. **Figure 5** reveals AES analysis results on the raw powder particles before and after XPS analysis. (a) and (b) correspond to Mg content of 0 and 1mass%, respectively. The upper results are before XPS analysis (as-received) and the lower are after the analysis (after heating). In both raw powder particles, the concentration of Sn is observed at the inner region of about 60nm in the depth from the particle surface. This means that the concentrating phenomenon of Sn elements at the inner region below the surface after heating is independent of the Mg content of the raw particles. The Al-Sn binary phase diagram [6] indicates that the melting point of Sn is 505K and the solubility limit of Sn in Al at the eutectic temperature (501K) is about 0.5mass%. Accordingly, Sn element of 1mass%, which is dissolved in the matrix of the raw particle by the rapid solidification process, changes to a liquid state during heating to 825K, and it moves and concentrates at the inner region below the particle surface. **Figure 6** shows a dependence of the photoelectron spectrum intensity on the heating temperature. (a), (b), and (c) correspond to the Mg content of 0, 0.5 and 1mass%, respectively. Figure 6 (a) indicates no change in the intensity of Al[O], Al[M] and Mg2p photoelectron spectra for a constant of Sn3d spectrum intensity. As shown in Fig. 6 (b) and (c), that of Sn3d photoelectron spectrum suddenly increases at the temperature range from 670K to 700K. On the other hand,

the temperature coincides with that of increasing the Al[M] intensity. Based on these results, it is suggested that Sn in a liquid state appears at the particle surface simultaneously after the appearance of Al[M] via deoxidization of the Al_2O_3 surface films. Therefore, Mg is necessary for the local appearance of Sn in a liquid state at the aluminum alloy particle surface during heating.
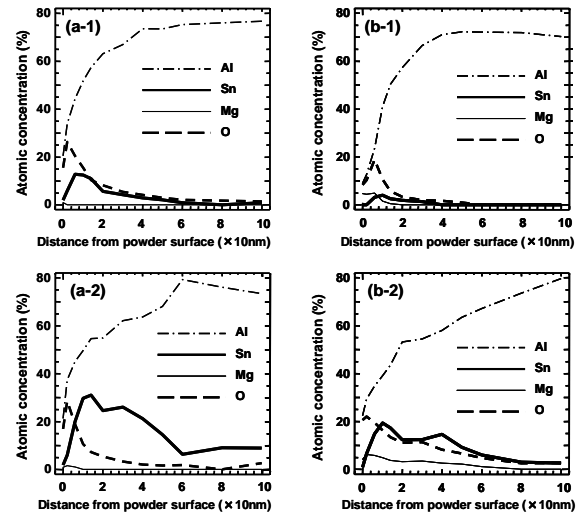

Fig.5 AES analysis results on as-received raw powder (-1) and heated to 823 in XPS analysis (-2). Mg content; 0% (b) and 1% (b).
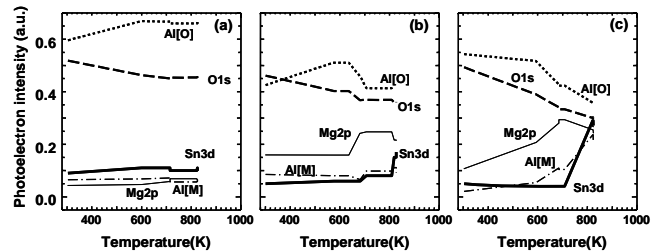

Fig.6 Relationship of photoelectron intensity changes in between Al[M] and Sn3d spectra during heating to 825K. Mg content; 0% (a), 0.5% (b) and 1% (c).

Figure 7 schematically illustrates the behavior of Sn and Mg on the topmost surface of the aluminum alloy powder particle during heating, and is considered by the following mechanism. At the early heating stage, Sn dissolved in the matrix diffuses, and moves to the particle surface. It locally concentrates in a liquid state at the inner region below the Al_2O_3 surface films over its melting point of 505K (a-1 and b-1). In the presence of Mg, the oxidization of Al_2O_3 films by Mg occurs over 670K and the Al_2O_3 surface films are locally destroyed (a-2). During heating to 825K, Sn in a liquid state appears at the particle surface through the cut Al_2O_3 films simultaneously with Al in the metallic state (a-3). On the other hand, when Mg is not present in the particle, Sn in a liquid state does not appear at the particle surface and exists at the inner region below the Al_2O_3 surface films

after heating over 670K due to no deoxidization phenomenon by Mg (b-2 and b-3).
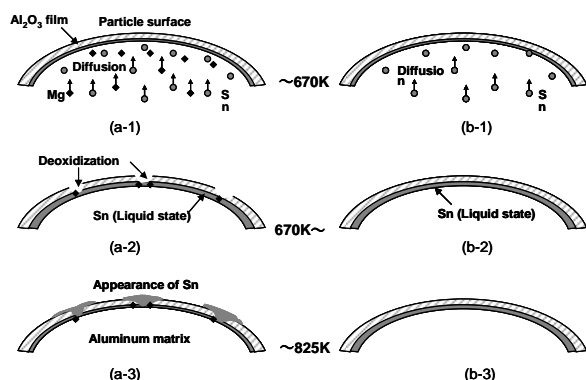

Fig.7 Schematic illustration of appearance of Sn liquid phase at particle surface during heating in using aluminum alloy powder containing Sn with Mg (a) and without Mg (b).

4. Conclusion

(1) The intensity of the Sn3d photoelectron spectrum increases with increases in the Mg content of aluminum alloy powder at elevated temperatures over 700K.

(2) Sn dissolved in the matrix of the raw particle diffuses to the particle surface as a liquid state by heating over 505K, and concentrates at the inner region of about 60nm in the depth from the surface. This phenomenon is independent of the Mg content of the raw particles.

(3) Sn in a liquid state appears at the particle surface simultaneously with Al in a metallic state after the deoxidization phenomenon of Al_2O_3 surface films. The temperature is from 670K to 700K approximately.

(4) Mg is necessary for the local appearance of Sn in a liquid state at the particle surface during heating.

References

1) L. S. Darken and R. W. Gurry: Physical Chemistry of Metals, McGraw-Hill, New York (1953).

2) A. Kimura et al: Reduction mechanism of surface oxide in aluminum alloy powders containing, Applied Physics Letters, 26 (1997), 3615-3617.

3) K. Emura et al: Superconducting storage ring NIJI-III, Rev. Sci. Instrum., 63 (1992), 753-755.

4) K. Kondoh et al: Mechanical and Wear Properties of In-Situ Directly Nitrided Sintered Al-AlN Composite Material, Journal of the Japan Society of Powder Metallurgy, 46 (199), 1044-1052.

5) K. Kondoh et al: Surface Reaction Analysis by X-Ray Photoelectron Spectroscopy Using Synchrotron Radiation and Microstructure Analysis of AlN Layer Produced by In-Situ Direct Nitriding Process, Journal of the Japan Society of Powder Metallurgy, 46 (199), 801-810.

6) M. Hansen, Constitution of Binary Alloys (Second Edition): Metallurgy and Metallurgical Engineering Series, McGraw-Hill, New York (1958).

33