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FABRICATION AND MICROSTRUCTURES OF Al-Li ALLOY PARTICLE-FILMS BY RF-PLASMA TECHNIQUE

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ABSTRACT

The influence of rf-plasma operation on the thin film formation containing small particles for Al-Li alloys mainly have been studied as a function of Ar gas pressure and plasma power by means of a 200kV transmission electron microscope (TEM). Under the non-plasma operation, the transition from continuous thin films to clusters of grape-like small particles occurred at Ar gas pressures above 20Pa. Particles were single crystals with clear crystal habit planes. Under the plasma operation, the influence of gas pressures on the film formation at a plasma power of 5W was also examined. Thin films containing particles below 30Pa and the films containing mainly particles above 40Pa were formed. The prominent change of the average particle size was not recognized. The increase of the plasma powers at 20Pa, which formed particles under non-plasma, suppressed growth of particles, and homogeneous films containing very small particles were fabricated. The electric conductivity showed slight decrease with an increase of plasma power.

INTRODUCTION

Since theoretic work on electric and magnetic properties of fine particles had been reported by Kubo[1], Kimoto et al.[2,3] energetically have studied fine particles prepared by the evaporation in inert gases atmosphere, which might be possible to certify Kubo's theory. Fine particles of pure metals and alloys have been attracting special attention owing to above reasons. Therefore, the present work was mainly conducted to develop the fabrication method of thin films containing the fine particles and clusters of fine particles. Hereafter, we describe them as "particle-film". Al is easily possible to make fine particles[2-4]. The present author has investigated mechanical properties and neutron-irradiated defects of Al-Li and Al-Mg-Li alloys as one of candidate materials for D-T burning devices of fusion reactor[5,6]. Therefore, Al-Li alloy and pure Al alloy as raw materials of the evaporation were selected to obtain fundamental knowledge on the influence of the plasma operation. This paper reports mainly the influence of plasma operation power and Ar gas pressure under plasma operation on particle-films formation.

EXPERIMENTAL PROCEDURE

Particle-films were fabricated by use of a basic plasma-kit (BP-1, Samco International Inc.)[7,8]. This system consists of a Pyrex bell jar, one pair of parallel electrodes of 0.08m (upper) and 0.10m(lower) in diameter, and a tungsten filament of basket type for electric resistance-heating evaporation of Al-Li alloy and Al. Distance between electrodes was about 0.1m. The basket filament set beside electrodes. The apparatus was connected to an FRG-200 rf-generator operating with a matching network at 13.56MHz, to gate valve for introducing Ar gas, to rotary pump and diffusion pump, and to the power control unit for the tungsten filament. The reactor chamber was initially evacuated to about 2×10^{-2} Pa. Ar gas (99.999%, purity) was induced in this vacuum through needle valve at various gas pressure levels. Al-2.28wt.%Li alloy and pure Al (99.999%, purity) as raw materials were used. Under plasma operation, Ar gas pressures were varied in the region between 10 Pa and 60Pa at a constant plasma power of 5W. Plasma powers were selected between 5W and 10W at 10Pa and 20Pa. Deposition rates was almost constant ~1nm/s.

Microstructures and crystallographic structures of particle-films were investigated by using TEM's image and its selected area diffraction (SAD) patterns, respectively. The used TEM was 200kV(JEM 2000FXII, JEOL). Cu and Mo meshes of 3mmϕ covered with collodion film as the substrate, KCl single crystals, or glass substrates were used depending on the purposes. The annealing effects on microstructures of particle-films were studied by using double tilt heating holder (Model 652-Ta, Gatan Inc.). The annealings were carried out in situ experiment in TEM.

The sheet electric conductivity of the thin films was measured with coplanar electrodes of aluminum in air by using an electrometer (HA-501, Hokuto-denki Co.). The details of measurement were reported in other paper[8].

RESULTS AND DISCUSSION

The present paper describes mainly results obtained with the evaporation of Al-2.28wt.%Li alloy as a raw material.

Non-plasma operation

The influence of Ar gas pressures between 0.1Pa and 600Pa on the formation of particle-films for Al-Li alloys were investigated. Thin films were formed below 10Pa, small particles above 20Pa. Similar results were also obtained with pure Al. However, lattice constants of Al-Li alloys showed low values in comparison with those values of pure Al in the pressure range between 0.1Pa and 100Pa[7]. This fact suggests that Li atoms are existing in Al lattice. Above 100Pa, the size of particles increased with an increase of gas pressure. It became about 200nm in diameter at 600Pa. Particles had clear crystal habit planes above 200Pa. This result agreed with one obtained by Kimoto and Nishida[3], and Sun et al.[4] Fig. 1 shows a typical example of Al-Li particles prepared at 600Pa. It should be noted that particles have habit planes.

Plasma operation

Influence of Ar gas pressure The influence on the film formation at gas pressures of 10Pa, 20Pa, 40Pa and 60Pa were investigated at constant plasma power of 5W. Fig.2 shows examples of TEM's bright field (BF) images and their SAD's patterns of thin films prepared at 10Pa and 60Pa. Film thicknesses were approximately 60nm. As seen in Fig. 2 (A), small and large particles existed in thin films. Average sizes of small and large particles were about 10nm and 50nm, respectively. It should be noted that large particles as seen in Fig. 2 (B) are composed of particle clusters, and they increase in comparison

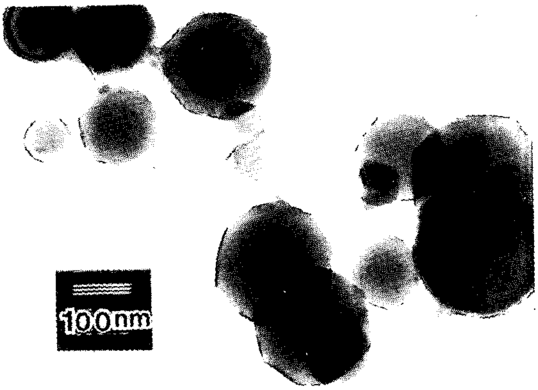

Fig. 1. Al-Li particles prepared at 600Pa.

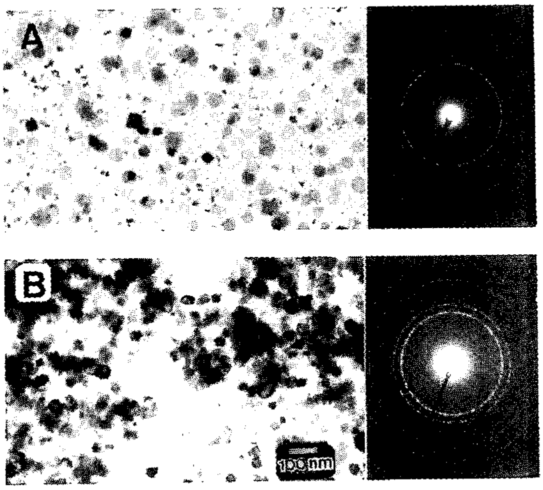

Fig. 2. The influence of Ar gas pressures on the formation of thin films and particles. TEM's photographs show bright field images. Plasma power was kept at constant value of 5W. A ; 10Pa, B ; 60Pa

with those in Fig. 2 (A). On the other hand, small particles as seen in Fig. 2 (A) decrease. This may indicate that growth of small particles proceed, and large particles increase. Above 40Pa, large particles each other were overlapping as seen in Fig. 2 (B). As seen in SAD's pattern of Fig. 2(B), spots on diffraction rings increased in comparison with those of Fig. 2 (A). This suggests that large particles increase. The formation of particle clusters at constant gas pressures was resemble to the result under the non-plasma operation.

Influence of plasma power;For two cases of constant pressures of 10Pa and 20Pa, the influence of plasma power between 5-20W on particle-films was investigated. Under non-plasma, films were formed below Ar gas of 10Pa and grape-like particles above 20Pa. At constant pressure of 10Pa, plasma powers were changed between 5-20W. TEM's images were not shown in the present paper, it was found that particle size in films became small with the increase of plasma power. Fig. 3 shows TEM's images (BF) at pressure of 20Pa and SAD's patterns. A, B and C in the figure show the results of 0W, 10W and 15W, respectively. As seen in Fig. 3, the particle size decreased gradually with the increase of plasma power.

Diffraction patterns also showed a good correspondence to the change of particle size. For the plasma power range from 5 to 20W, the increase of plasma power suppressed growth of particles. And homogeneous thin films containing fine particles below 10nm in diameter were formed. Fig. 4 (A) shows the relationship between the average particle size and the plasma power (-■-),together with

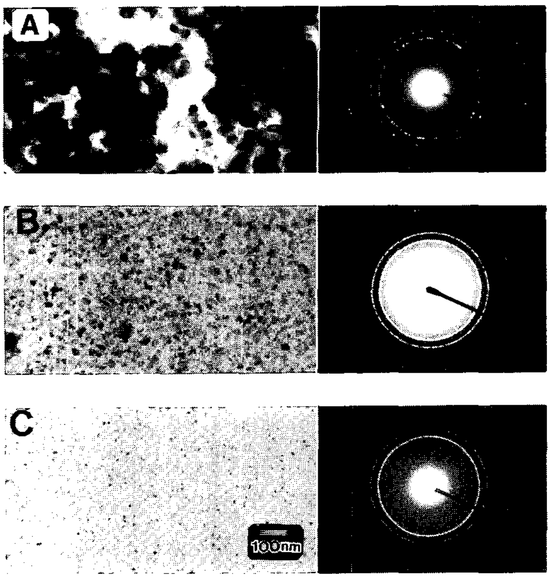

Fig. 3. The influence of plasma powers on the formation of thin films and particles. Ar gas pressure was kept at 20 Pa. A ; 0 W, B ; 5W, C ; 15W

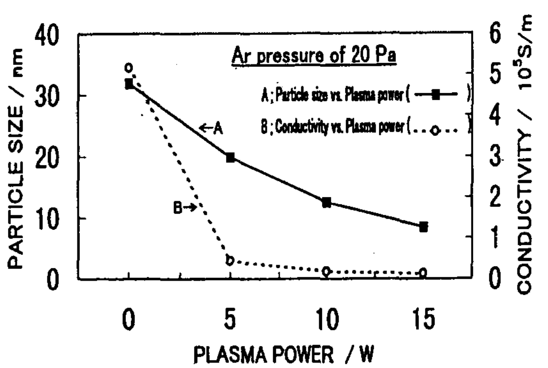

Fig. 4. The relationships between average particle size and plasma power (-■-), and between electric conductivity and plasma power (-○-). All specimens were prepared at Ar gas pressure of 20Pa

the relationship between the electric conductivity and the plasma power (-○-).

Electric conductivity Electric conductivity of particle-films prepared by various experimental conditions were measured. A part of prepared films was difficult to measure the electric resistivity. Because Al-coatings to measure the film thickness were difficult for grape-like particle-films at high Ar pressures. The change of electric conductivity against plasma power at a constant pressure of 20Pa are shown in Fig. 4(B) (-○-). The electric conductivity extraordinary decreased from 5.5×10^5S/m for 0W to 4.4×10^4S/m for 5W. It gradually decreased above 5W as seen in Fig. 4(B) from 4.4×10^5S/m to 1.2×10^4S/m. The decrease of electric conductivity against the plasma power can be interpreted by the following reasons. Namely, the increase of plasma power divide large particles into more fine particles as seen in Fig. 3, they distribute homogeneously in the thin film. As this results, contact area between particles with irregular shape and the matric film increases. Such contact boundaries work as obstacles of electron motion. From the analysis of SAD's patterns, it was found that the lattice constant of film prepared under the non-plasma was 0.403 nm, and values of all specimens prepared under plasma operation showed larger values. This suggests that many Ar atoms during the formation of films are introduced in the films. This also may contribute to the increase of electric resistivity. As-grown particles in thin films and grape-like particles generally not changed their structures and the size between 300K and 724K by in-situ annealing in TEM. They were comparatively stable.

SUMMARY

In the present work, mainly the influence of rf-plasma operation on the film formation containing small particles for Al-Li alloys has been studied as a function of Ar gas pressure and plasma power by means of TEM and by the measurement of electric conductivity. Main results are summaries as follows.

Under the non-plasma operation, the transition from the continuous thin films to the cluster of grape-like small particles occurred at gas pressures above 20Pa for Al-Li alloys and pure Al. The particles were single crystals. They had clear crystal habit planes above 200Pa.The size of particles increased with an increase of gas pressure.

The influence of gas pressure in the region of 10-60 Pa at plasma power of 5W on the formation of thin film was examined. At low pressures below 30Pa, thin films containing particles were fabricated. Above 40Pa, films containing mainly particles were formed. The prominent change of particle size was not recognized.

The influence of plasma powers at 20Pa between 5-20W on the formation of films were investigated. An increase of plasma power suppressed the growth of particles contained in films, and homogeneous films containing very small particles were produced.

Electric conductivity extraordinary decreased from 5.5×10^5S/m for 0 W to 4.4×10^4S/m for 5W. The conductivity gradually decreased with an increases of the plasma power from 4.4×10^4 S/m to 1.2×10^4 S/m. This decrease is explained as the increase of contact area between particles and film matrix, and also as the result of induction of Ar gas in the film.

It is concluded from the present work that the plasma operation is effective to fabricate the thin films containing small particles below 10nm.

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