전류의 파형 변화에 의한 알루미늄 에치 터널의 성장 거동

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RESUMPTION OF ALUMINUM ETCH TUNNEL GROWTH AFTER CURRENT INTERRUPTIONS

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INTRODUCTION

Aluminum etch tunnels are micron-wide corrosion pits which are formed during anodic etching in chloride ion - containing solutions, at temperatures higher than 60℃(1;2). Tunnels penetrate the metal along <100> crystallographic directions. Metal dissolution occurs from the tunnel tip, or end surfaces, at current densities on the order of 10A/cm^2; the rate of corrosion on the tunnel sidewalls is very small by comparison, apparently because of the presence of a passive oxide film. Length:width aspect ratios of tunnels can approach 100:1. Tunnel etching is carried out industrially, in the manufacture of electrodes for high-voltage aluminum electrolytic capacitors.

The corroding tip of an etch tunnel provides an experimentally convenient surface for the study of oxide film passivation, since passivation usually stops or alters tunnel growth, and these effects are apparent from the tunnel morphology. Tip passivation can occur in response to current interruptions during etching(1). These interruptions are sometimes used in commercial etching processes, since they can produce abrupt changes in the direction of tunnel growth. However as shown presently, if the interruption time is shorter than about 10 ms, tunnel growth continues despite interruptions. Tak and Hebert(3) showed that, when the applied current was stepped to zero durung etching, an oxide film formed on the tunnel tip in a time of less than 100μs. Evidently this oxide film could be removed when the interruption time was short enough. In the present communication, the recovery of active area on the tunnel tips is characterized, using observations of the tip surface topography by scanning electron microscopy. Also, experiments with cyclic current interruptions were used to determine the time necessary for recovery of active dissolution, after an interruption of a given time.

EXPERIMENTAL

The apparatus and procedures for etching have been described in detail previously(5). Aluminum electeodes were 99.98% pure foils. Before etching, they were pretreated by immersion in 1.0N NaOH at room temperature for 20 minutes. The etchant bath was 1.0N HCl, at 65℃. Etching current was applied with a potentiostat (PAR 273). In the case of experiments in which single anodic current pulse were applied after interruptions, the interruption was after etching for 5s at a constant current of 40 mA/cm^2. The curent waveform for these experiments was supplied to the potentiostat by a personal computer, via a GPIB-PC interface. In other experiments, repetitive current cycling waveforms were supplied by a pulse generator (Datapulse). The morphology of etched surfaces was observed by forming oxide replicas of these surfaces(5), and examining the replicas with a scanning electron microscope (JEOL JSM 840).

RESULTS AND DISCUSSION

When anodic current pulses are applied after interruptions, small pits were observed to form on the tip surfaces, when the pulse time is as small as 20 ms(4). The number of these pits decreased as the interruption time increased. Potential transients were analyzed to show that sudden increases of faradaic durrent, which accompanied the appearance of these pits, occurred at times less than 1 ms after the interruption.

As etching continued for still longer times after the current interruption, the pits became larger, by dissolution and merging with adjacent pits. Experiments with anodic pulse times of several seconds showed that eventually, one or more of these pits began to grow as a tunnel, apparently because of passivation of its sidewalls. When the interruption time was less than about 10 ms, the entire tunnel tip surface was ultimately reactivated. The resulting tunnels appeared identical to tunnels grown for the same total etching time with no current interruption. However, when the interruption time was longer than 10 ms, the tunnels showed constrictions at positions along their lengths corresponding to the time of the current interruption (Fig1).

Current cycling experiments were carried out to measure the critical pulse time for complete reactivation of the tip surface, for a given interruption time. The applied current was held constant for a period of 5s, and was then stepped to a lower value. Less than one second after this step, current cycling was began, and continued for a period of 5s. The individual current cycles consisted of a time (t_L) at zero current followed by a time (t_H) at the original current. The purpose of the current step prior to cycling was to passivate part of the tunnel tips, thereby producing sharp constrictions in the tunnel width(1;5). These constrictions served to mark the position along the tunnel length at which current cycling had been initiated.

Depending on the values of t_H and t_L, tunnels either grew continuously during current cycling, or else stopped growing shortly after cycling began. Fig. 2 shows that, for a given interrution time, tunnels grow during cycling only when t_H was greater than a certain value, which is referred to here as the reactivation time, t_R. t_R increased with increasing t_L. Apparently, when t_H was less than t_R, the active tunnel tip area was not totally recovered in the first cycle, so the tunnels entered the second cycle with part of their tip area passive. With further cycles, the passivated area on the tip accumulated, until finally, the entire tip was passive. Tunnel death was also accompanied by the appearance of clusters of small pits near the tunnel tip or on the external surface, similar in appearance to the pits formed during ac etching of aluminum(6). These pit clusters were evidently formed in the succeeding cycles after tunnel death. When t_L was larger than 8 ms, tunnels could not be reactivated for any t_H. This time agrees closely with the critical interruption time of 10 ms noted previously in the discussion of single interruptions, above which the entire active tip surface could not be reactivated for any t_H.

The recovery of tunnel growth after interruptions is a result of growth and merging of pits, which formed on the tip at the beginning of the anodic current pulse. As noted above, the time for pit nucleation is less than 2 ms, and the number of pits is inversely related to the interruption time. When the interruption time (t_L) is small, the average distance between pits on a given tip surface is small, and conseqently the time for pits to grow together(the reactivation time, t_R) is short. A larger t_L increases the average interpit distance, and hence t_R. If t_L is made sufficiently long (> 10 ms), apparently the sidewalls of pits passivate before they have time to merge. The further growth of these pits is in the form of individual etch tunnels.

CONCLUSIONS

Current interruptions of a few milliseconds during anodic etching passivate the corroding tip surfaces of aluminum tunnels. The recovery of active dissolution after interruptions occurs by the initiation and expansion of small pits on tunnel tips; eventually, these pits merge and cover the tip surface. The complete reactivation of the active tip area requires a few tens of milliseconds. When the interruption time is increased, the number of pits nucleated on the newly passivated tip surface decreases. Consequently, the reactivation time increases.

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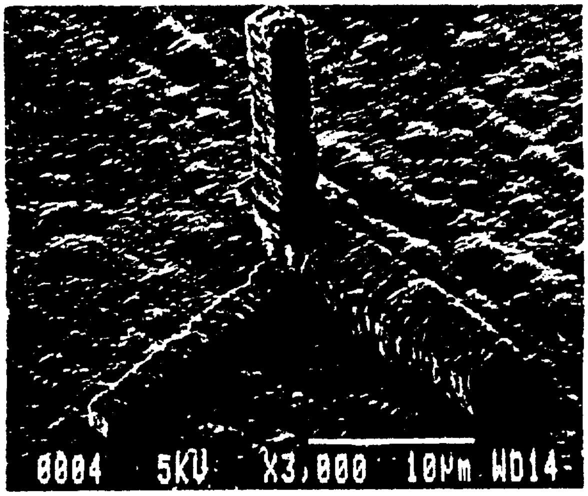

Figure 1. Scanning electron micrograph of an oxide replica of an etched surface, showing the effect of passivation caused by a current interruption. An interruption of 12 ms was applied after etching for 5s at 40 mA/cm^2. Subsequent to the interruption, etching was continued at this current density for another 5s.

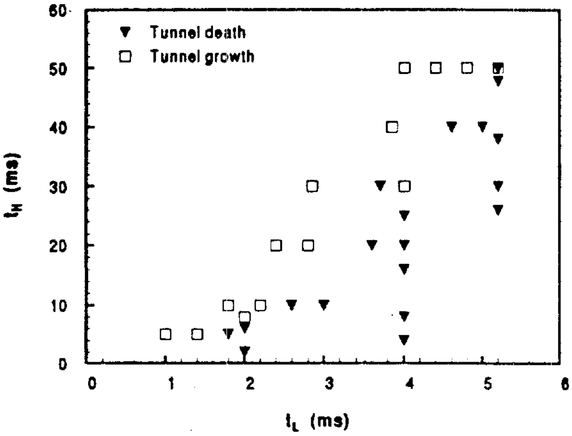

Figure 2. The relationship between the current interrupyion time (t_L), and the anodic current pulse time (t_H), for either contiuous tunnel growth or tunnel death, during current cycling experiments. Each cycle consisted of a current interruption followed immediately by a current pulse. The anodic current during the pulse was 40 mA/cm^2.