Solutionizing Effects during Corrosive Wear in 6061 Aluminum and Composites

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Samples of commercial 6061 aluminum alloy in both the monolithic form and reinforced with 0.1 and 0.2 volume fraction of alumina particles were solutionized for 5, 10, and 20 h at 540 °C. A transient current generated in the composite material as a result of continuous and impact scratching during the corrosive wear process shows that composites are more sensitive to the microstructural changes taking place during solutionizing than is the monolithic 6061 alloy. The increase in grain size in the alloy during solutionizing does not significantly affect the transient current. Decohesion of the particles in the composites increases the interfacial area, and this interfacial region may act as an anodic site for corrosion to occur. Dislocations generated due to differences in the coefficient of thermal expansion values for alumina particles and aluminum matrix increase the measured transient current.

Keywords	coefficient of thermal expansion, corrosion,
	passivation, solutionizing, transient current, wear

1. Introduction

When the surface of a metal in a corrosive environment is scratched, bare metal is exposed and reacts with the electrolyte. The metal may be in a passivated state when the process of scratching ruptures the film on the surface (called depassivation), resulting in a surge of current. This is called transient current, the magnitude of which indicates the amount of corrosion taking place. Unless the surface film is destroyed by some other mechanical means, it can be assumed to repassivate.

Depassivation and repassivation processes may continue for a long period of time in instances where the metal is being continuously scratched against a hard object during motion (i.e., corrosive wear). Corrosive wear of metals and alloys can result in large amounts of waste in an industrial environment.

This study compares the transient current response (TCR) from the surfaces of composites of 6061 aluminum alloy reinforced with alumina particles and the alloy in its monolithic form when subjected to two types of scratches: impact and continuous. The microstructural features controlling the TCR are examined by varying the amount of solutionizing time for both the composites and the monolith.

2. Scratch Technique

The scratch technique has been used extensively to study the corrosive wear behavior of some of the ferrous materials from the Fe-Cr-Ni alloy system (Ref 1-10). Burstein et al. (Ref 11-17) have used a rotating disk electrode method to present both theoretical and experimental results for the corrosive wear of titanium and ferrous materials by scratch testing in alkaline solutions.

The scratch technique used in this research consists of dropping a stylus containing a Vickers hardness indenter onto the surface of an immersed rotating cylindrical electrode and measuring the transient current between the sample and a calomel electrode. The important experimental variables include load on the stylus, strength of the electrolyte (usually containing equal molar ratios of KCl and H_2SO_4 solutions), electrode rotation speed, grain diameter, microconstituents in the metal, and other metallurgical factors associated with the microstructural details. Increasing the load on the stylus increases TCR, which is insensitive to electrode rotation speeds up to 1500 rev/min (Ref 4-9). Electrolyte strength plays an important role through the conductivity of the solution, and it has been shown that increasing the concentration of sulfuric acid increases the TCR for the same reason (Ref 3).

A recent study (Ref 1) on Fe-18Cr-5Ni alloy and type 304 stainless steels indicates that the forms of TCR in impact and continuous scratches differ considerably from each other. The transient current attains a maximum value when the stylus tip leaves the electrode surface after an impact. It stabilizes to a maximum value during the continuous scratching process. Thus, continuous scratching allows a balance between repassivation and depassivation to take place until such time when the stylus ceases to make contact with the electrode. It has been found that the TCR value is higher in the continuous scratching process compared to that evolved in the impact mode of wear for similar loads (Ref 3, 4, 6, 9, 10).

The grain size effect on TCR was assumed to be such that if the grain boundaries are anodic compared to the matrix, then decreasing the grain size must increase the TCR value, which is consistent with previous studies on Fe-Cr-Ni alloys (Ref 3). Comparing the TCR between the ternary Fe-Cr-Ni alloys and type 304 stainless steels reveals that twin boundaries in type 304 significantly contribute to TCR (Ref 1). Other microstructural features such as dislocations present in a randomly distributed or cellular structure and slip bands result in different corrosive wear behavior in ferrous alloys (Ref 1).

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3. Experimental Details

Composite materials containing 0.10 and 0.20 volume fraction of alumina particles (VFAP) distributed in a matrix of 6061 aluminum alloy were purchased from Duralcan Inc.; the specifications stated the particle sizes to be 10 and 20 μ m, respectively. A commercial-grade 6061 aluminum alloy was purchased from a local warehouse.

The composites and the monolith were machined to produce cylindrical electrodes measuring 12.5 mm, with inner and outer diameters of 6.35 and 12.5 mm, respectively. A polarization scan of the electrodes in a solution consisting of 0.1 *M* NaCl in distilled water revealed the pitting potential to be nearly -1150 mV, using a standard calomel reference electrode, when the rotation speed of the electrode was 1500 rev/min. The corrosive wear experiments were performed at -850 mV. It must be



Fig. 1 Validity of grain growth law in 6061 aluminum alloy (a) and composites of 6061 aluminum alloy reinforced with alumina particles (b) at a solutionizing temperature of 540 $^{\circ}$ C

noted that the rotation of the electrode causes the temperature of the electrolyte to rise from 20 to 55 $^{\circ}$ C, but remains constant throughout the experiment.

The electrolyte cell was made of Teflon (E.I. DuPont de Nemours & Co., Inc., Wilmington, DE) with an attachment to connect the electrode sample to a motor to provide a constant rotational speed. Silver brushes minimized electrical noise. The stylus, containing a Vickers hardness indenter at its tip, was dropped from a known height and connected to a load cell whose output was interfaced to a computer to record transient loads during impact. In addition to the standard calomel reference electrode, the cell was connected to the potentiostat with the help of a platinum cage counterelectrode wound around the cell. A salt bridge containing a saturated solution of potassium sulfate was placed between the cell and the reference electrode to prevent the migration of chloride ions into the cell.

Purified argon gas was used to flush the electrolyte at least half an hour before the experiment and throughout the entire test. The transient loads and the currents were simultaneously recorded on a computer.

The as-machined samples were solutionized in a box furnace at 540 °C for 5 to 20 h in air. The solutionized samples were polished again, up to 0.3 μ m finish, to remove oxidation effects from the surface. The samples were stored in a refrigerator to prevent natural aging.

Electrodes subjected to both impact and continuous scratching were examined in a scanning electron microscope (SEM) to observe topographical features of the scratches. Adherence characteristics—related to the bonding between the alumina particles and the matrix—were also studied for the composite materials.

4. Results and Discussion

The grain growth law states that the square of the grain diameter is proportional to the time of solutionizing. The composites containing 0.1 and 0.2 VFAP and the 6061 aluminum in its monolithic form follow the grain growth curves shown in Fig. 1. Note that the slope for the alloy is much higher than those for the composites. Comparing the composites, the slope is smaller for the one containing a higher volume fraction of alumina particles. This clearly indicates that the particles inhibit grain growth during the solutionizing process.

4.1 6061 Aluminum Alloy

Figure 2 shows the TCR of the monolithic 6061 aluminum alloy during impact scratching. The current values indicate that as solutionizing time increases, peak current increases. However, the increase in current value is not very significant compared to that obtained during continuous scratching. As shown in Fig. 3, current values of 0.8, 1.25, and 1.4 mA can be obtained in this alloy for solutionizing times of 5, 10, and 20 h, respectively.

Even though the TCR also has been measured on the as-machined samples and indicated in Fig. 2 and 3, these values cannot be used to analyze the effect of solutionizing time on corrosive wear behavior in the present case. Their inclusion throughout this paper is for reference purposes only. The microstructural features affecting corrosive wear behavior due to solutionizing are quite different from those in the as-machined condition. The material was supplied in the extruded form, which consists of deformed structure, whereas the solutionized samples have been assumed to be recrystallized even for the shortest solutionizing time of 5 h. Thus, this alloy shows less sensitivity toward solutionizing during impact than during continuous scratching.



Fig. 2 TCR during impact scratching, in a 0.1 *M* NaCl electrolyte, for the 6061 aluminum alloy: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h

All transient current graphs in this paper include two characteristic features of depassivation and repassivation. The initial increase in current corresponds to the generation of electrons when the stylus first strikes the rotating electrode and breaks the protective film. After the stylus leaves the surface of the electrode, the current falls off due to the reformation of film, called repassivation. The plateau obtained in the TCR from the continuous scratches is perhaps due to the existence of a bal-



Fig. 3 TCR during continuous scratching, in a 0.1 *M* NaCl electrolyte, for the 6061 aluminum alloy: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h

ance between the simultaneous processes of depassivation and repassivation during the experiment.

Figure 4 shows SEM micrographs of scratches produced during the impact experiment, clearly indicating the presence of diamond shapes for the four cases. The impression of the Vickers hardness indenter is also quite apparent. However, the continuous scratches shown in Fig. 5 reveal more plowed material in aluminum alloys and its composites than was observed in the previous study involving Fe-Ni-Cr alloys (Ref 1). This can be attributed to differences in hardness between the two types of materials. The aluminum alloys are soft. When the stylus hits the electrode, the deeper indentation prevents the stylus from vibrating; hence, a single-track indentation channel results. Several tracks were observed in similar experiments performed with Fe-Ni-Cr alloys (Ref 1).

4.2 Composite with 0.1 VFAP

Figures 6 and 7 show the TCR from the composite of 6061 aluminum alloy reinforced with 0.1 VFAP during impact and

continuous scratching, respectively. This composite material shows a definite increase in peak current values as a function of solutionizing time. An increase in current value from 0.09 to 0.25 mA corresponding to an increase in solutionizing time from 5 to 20 h is an indication of the higher extent of corrosion taking place during impact testing. Recall that the monolithic alloy was found to be almost insensitive to solutionizing times with respect to the peak current values (Fig. 3). Also, the continuous scratches show an increase in peak current values from 0.85 to 1.3 mA for an increase in solutionizing time from 5 to 20 h. The magnitude of the observed current values during impact and continuous scratching reveals that continuous scratches always produced higher current for a similar solutionizing treatment time.

Figure 8 shows SEMs of the impact scratches observed in the 0.1 VFAP composite at different solutionizing times. Scratch size increases with increased solutionizing time. (It might first appear that the scratch for a solutionizing time of 10 h is much larger than the other scratches in Fig. 8, but note that



Fig. 4 Morphology of the impact scratches, in a 0.1 *M* NaCl electrolyte, in 6061 aluminum alloy as a result of corrosive wear: (a) as machined and after solutionizing at 540 $^{\circ}$ C for (b) 5 h, (c) 10 h, and (d) 20 h. (Art has been reduced 77% for printing)

this micrograph [Fig. 8c] is simply shown at a higher magnification than the others.) Another notable feature in Fig. 8 is the density of particles (number of particles per unit area observed in such micrographs). The density of particles appears to be much smaller inside the scratches compared to outside. This could be an indication of particle pullout during the corrosive wear process. The continuous scratches shown in Fig. 9 indicate the presence of almost a single track in each case, and particles inside the tracks cannot be identified easily.

4.3 Composite with 0.2 VFAP

The TCRs in Fig. 10 and 11 show the corrosion behavior of 6061 aluminum alloy reinforced with 0.2 VFAP during impact and continuous scratching experiments, respectively. An increase in peak current from 0.19 to 0.22 mA occurred for impact scratching for samples solutionized for 5 and 10 h, jumping to 0.6 mA when the composite was solutionized for 20 h. The continuous scratches, however, exhibited unusual behavior. As shown in Fig. 11, peak current values were insensi-

tive to solutionizing time. It is possible that in this composite the potential anodic sites were removed during either the solutionizing treatment or the dynamic recovery taking place during the corrosive wear treatment. Large VFAP can induce sufficient dislocation density generation to cause the dynamic recovery to be effective enough to place the dislocations in a low-energy configuration, where its potential to be an anodic site diminishes considerably.

Figure 12 shows SEMs of impact scratches observed in the 0.2 VFAP composite. One striking feature: The alumina particles of the composite are retained in the matrix within the scratch itself even after wear from the stylus. In another study of the same composite (Ref 18), the bonding between the particles and the matrix improved with increasing solutionizing time. Consequently, when tested under tension until failure, the particles detached themselves from the matrix when solutionized for shorter times. The density of particles held intact in their fracture surfaces when the composite was solutionized increased with an increase in solutionizing time. The results of Fig. 12 do not indicate such features.









0.10 YFAP **Transient Currents of Impact Scratches**

Fig. 6 TCR during impact scratching, in a 0.1 M NaCl electrolyte, for the 6061 aluminum alloy reinforced with 0.1 VFAP: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h



Fig. 7 TCR during continuous scratching, in a 0.1 *M* NaCl electrolyte, for the 6061 aluminum alloy reinforced with 0.1 VFAP: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h

Figure 13 shows the continuous scratches developed in this composite. Details of the features of these scratches were similar to those observed for the monolithic 6061 aluminum alloy and the composite containing 0.1 VFAP.

4.4 Analysis

The transient current values during impact experiments as a function of solutionizing time are reproduced in Fig. 14 for the three tested materials. The data points represent the average values of the transient current from several experiments for a given solutionizing time, whereas the transient current graphs shown earlier were typical examples of corrosive wear behavior. Figure 15 is the same graph as Fig. 14 except that current density, instead of current, is plotted as a function of solutionizing time. The current density was computed by dividing the current values by the area of the scratches as measured on the SEM micrographs. The data points in Fig. 15 include the average current values, shown in Fig. 14, divided by the average areas of scratches from several experiments.

Several factors must be taken into account when analyzing data using current or current density (Ref 4). In this case, however, the authors do not see the problem normally encountered in the selection of the two parameters-current and current density-because the forms of the curves in Fig. 14 and 15 do not change. Figure 14 shows that the corrosive wear behavior of the composites is identical whether they contain 0.1 or 0.2VFAP under the experimental conditions of this study. The slopes of the two lines for the composites are identical. The only difference is that the composite containing a higher VFAP generates higher transient current compared to the composite with a lower VFAP. The monolith shows very little change in transient current value with solutionizing time, and it may thus be assumed that it is insensitive to the selected heat treatment of this study. An empirical relationship has been established to relate the transient current generation in the composite during impact experiments to the solutionizing time and volume fraction of alumina particles:

 $i = 0.009(t) + 0.96(V_{\rm f}) - 0.04$ (Eq 1)

h



Fig. 8 Morphology of the impact scratches, in a 0.1 *M* NaCl electrolyte, in 6061 aluminum alloy reinforced with 0.1 VFAP as a result of corrosive wear: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h. (Art has been reduced 77% for printing)



Fig. 9 Morphology of the continuous scratches, in a 0.1 *M* NaCl electrolyte, in 6061 aluminum alloy reinforced with 0.1 VFAP as a result of corrosive wear: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h. (Art has been reduced 77% for printing)

where *i* is current in milliamperes, *t* is solutionizing time in hours, and $V_{\rm f}$ is the volume fraction of the alumina particles. Equation 1 does not include the data points in Fig. 14 and 15 for a solutionizing time of zero (as-machined condition), for the reasons discussed earlier in this section.

The model in Fig. 16 can be used to explain the higher TCR from composites compared to the monolith. The alloy exhibits grain growth during the solutionizing treatment and, as shown schematically in Fig. 16, at longer solutionizing time the grain size is larger. The grain boundaries are considered to be effective anodic sites in Fe-Ni-Cr alloys (Ref 1). The increase in grain size alone, however, does not change the transient current values to any significant degree, so it can be assumed that in aluminum they do not contribute much to the current values.

The composite, on the other hand, contains alumina particles; these particles or the interface between them and the matrix can be considered potential anodic sites during the corrosive wear process. It has been shown (Ref 18) that the particles undergo decohesion during the solutionizing treatment, which simply increases the interfacial area and thus increases anodic sites and generates the transient current. This explains why higher current values may be expected in composites compared to the monolithic alloy.

In addition, dislocations are generated during the solutionizing treatment because of differences in the values of the coefficient of thermal expansion (CTE) between the particles and the matrix. The CTE dislocations are also anodic sites; thus, the composites have two additional anodic sites compared to the alloy in its monolithic form: (1) the interfacial area between the particles and the matrix and (2) CTE dislocations. The relative contributions of the two factors to the transient current cannot be extrapolated from the data obtained in this study. Transmission electron microscope studies on the nearsurface (close to the scratches) microstructural evolution may be quite helpful in further analysis.



Fig. 10 TCR during impact scratching, in a 0.1 M NaCl electrolyte, for the 6061 aluminum alloy reinforced with 0.2 VFAP: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h



Fig. 11 TCR during continuous scratching, in a 0.1 *M* NaCl electrolyte, for the 6061 aluminum alloy reinforced with 0.2 VFAP: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h



Fig. 12 Morphology of the impact scratches, in a 0.1 *M* NaCl electrolyte, in 6061 aluminum alloy reinforced with 0.2 VFAP as a result of corrosive wear: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h. (Art has been reduced 77% for printing)

5. Conclusions

The TCR of the monolithic 6061 aluminum alloy was found to be very different from the composites reinforced with 0.1 or 0.2 VFAP. The contribution of the grain boundaries to the transient current in the monolithic alloy appears to be insignificant in terms of the changes in grain diameter taking place during solutionizing.

The transient current generated from the composites in impact experiments increases linearly with solutionizing time. The almost identical slopes in the graph between the transient current (Fig. 14), or transient current density (Fig. 15), and the solutionizing time for the composites containing 0.1 or 0.2 VFAP indicates that similar corrosive wear mechanisms are operating under the experimental conditions of this study.

An empirical relationship was developed between the transient current generated in the composites during impact experiments, time of solutionizing, and volume fraction of alumina particles in order to predict the corrosive wear behavior. The higher transient current response in composites can be attributed to (1) the increase in the interfacial area between the particles and the matrix by decohesion of the particles and (2) the generation during solutionizing of CTE dislocations, which act as anodic sites.

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Fig. 13 Morphology of the continuous scratches, in a 0.1 M NaCl electrolyte, in 6061 aluminum alloy reinforced with 0.2 VFAP as a result of corrosive wear: (a) as machined and after solutionizing at 540 °C for (b) 5 h, (c) 10 h, and (d) 20 h. (Art has been reduced 77% for printing)

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Fig. 14 Variation in the transient current for impact scratching, in a 0.1 M NaCl electrolyte, with solutionizing time for the monolithic 6061 aluminum and for composites reinforced with 0.1 and 0.2 VFAP at 540 °C

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Fig. 15 Variation in the transient current density for impact scratching, in a 0.1 M NaCl electrolyte, with solutionizing time for the monolithic 6061 aluminum and for composites reinforced with 0.1 and 0.2 VFAP at 540 °C



Fig. 16 Model for comparing transient current generation in the monolithic 6061 aluminum alloy and in composites reinforced with different volume fractions of alumina particles