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COMMENTS ON A PAPER BY BAIK AND RAJ

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A number of papers involving the oxidation of aluminum alloys containing magnesium have been published. Seamans and Butler (1), for example, used electron microscopy to study the development of MgO and $MgAl_2O_4$ in several aluminum-magnesium alloys. The spinel, $MgAl_2O_4$, was the primary oxidation product in an Al-5% Mg alloy. They suggested that magnesium is depleted from the metal at the metal-oxide interface and thus forms the oxide crystals. Forsvoll and Foss (2) found a similar depletion of magnesium during the oxidation of Al-Mg alloys. Dobson et al. (3) used electron microscopy to follow the oxidation of thin foils of three aluminum-magnesium alloys. They found that dislocation loops formed by quenching grew with time at temperatures occasioned by surface oxidation. This indicated that the vacancies, which were injected into the metal during oxidation, created a vacancy supersaturation that assisted loop growth.

Baik and Raj (4) performed an internal friction study on an aluminum-5 wght % magnesium alloy containing 90 ppm copper and 1.26×10^3 ppm iron. The damping peaks for specimens annealed in air were reduced 50°C by heating the same specimens in vacuum. In fact, these investigators observed that this process was reversible. To explain these observations, they surmised that when the copper oxidized it formed copper oxide in the grain boundaries, and this increased the temperature of the damping peaks. Subsequent heating in a vacuum reduced the copper oxide to elemental copper. This heating was at a temperature high enough to allow the copper to diffuse from the grain boundaries and thereby improve the homogeneity.

Both aluminum and magnesium are very strong reducing agents, which are often used for the reduction of exotic metals. Grauer and Schomaker (5) calculated the oxygen partial pressure at 800°K for aluminum-magnesium alloys at equilibrium. For an aluminum-5% magnesium alloy, MgO is the oxide that will form. The partial pressure of oxygen in equilibrium with this alloy at 800°K is 10^{-64}. This indicates that aluminum and magnesium atoms have an extremely strong affinity for oxygen. Baik and Raj (4) determined for an aluminum-5% magnesium containing 90 ppm copper that $a_{Cu}^4 \cdot P_{O_2} = 4 \times 10^{-23}$. (In this equation, a_{Cu} is the activity of copper.) They assumed that $10^{-6} < a_{Cu} < 10^{-4}$. This means that $40 < P_{O_2} < 4 \times 10^{-7}$. By comparing these values with the data from Grauer and Shomaker (5), one is led to the conclusion that any copper present in the alloy used by Baik and Raj (4) at 583°K would have existed only in the elemental state. It is recognized that there is a temperature difference between the two experiments, but it is trivial when one considers the magnitude of the difference between the values of the partial pressure of oxygen. Had it been possible to oxidize copper in aluminum, then the Hoope's process (6) would not have been needed to reduce the impurity levels in aluminum to less than 10 ppm. Injecting oxygen into molten aluminum would have been sufficient to oxidize any copper impurity.

Biak and Raj (4) observed a precipitate, which vanished during beam heating. With 5 wght % magnesium in aluminum, the alloy would have formed significant amounts of Mg_5Al_8, because the solid solubility of magnesium in aluminum at low temperatures is low (7) (1.9 wght % at 100°C). Baik and Raj (4) stated that the temperature rise occasioned by beam heating would have influenced the thermodynamic equilibrium between copper oxide and aluminum. (Beam heating will cause a relatively small rise in temperature.) Fisher (8) developed an expression for beam heating that Leighly et al. (9) corrected. If it is assumed that Baik and Raj (4) used a 100 keV electron microscope with a beam current of 20μ amp, the worst case for beam heating would cause a temperature rise in an aluminum alloy of ~21°C. This would occur if the electron beam were near the crossover of the condenser lens and at the center of the electron microscope specimen.

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One is left with a need to understand the difference observed by Baik and Raj (4) between specimens heated in air and in vacuum. Because they did not specify the humidity level of the air that was present during the annealing process, one must assume that water vapor was present. Gel'man et al. (10) showed that substantial amounts of hydrogen are in solution in aluminum after the aluminum has been heated in water vapor. This results from the reaction: $2Al + 3H_2O \rightarrow Al_2O_3 + 6H$. When $P_{H_2O} = 2.4kPa$ which is the saturation of water vapor in air at 20°C, they found that the solubility of hydrogen in aluminum was roughly twice that observed in dry hydrogen at 1 atm (11). Heating the sample in a near perfect vacuum would remove the hydrogen very rapidly, hence the change in internal friction observed by Baik and Raj (4). In recently conducted experiments in which ESCA was used, a very large content of magnesium was observed in the surface oxide formed on an aluminum-500 ppm magnesium alloy (12) heated to 580°C in very dry air. This indicates that the depletion of magnesium from the alloy is significant and would have left a very large vacancy supersaturation.

Because uncertainties exist in the interpretation of Baik and Raj's results (4), the experiments should be repeated and the variables controlled to improve the understanding of the experimental results. Two approaches could be used:

1. The specimens could be heated in either very dry air or humid air to determine if hydrogen from the aluminum-water vapor reaction causes the experimentally observed changes in internal friction.
2. The specimens could be heated in a high purity inert gas, such as nitrogen or argon, either very dry or with water vapor present to determine whether hydrogen alone causes the change in the internal friction or oxidation plays a role.

A comparison of the internal friction results of the above experiments should explain the cause for the differences in internal friction observed by Baik and Raj (4) for specimens annealed in air and in vacuum.

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ADDENDUM: Reply received from Baik and Raj on February 28, 1983

Leighly has correctly pointed out that the p_{O_2} in our experiments was never low enough to reduce the oxides of magnesium and aluminum, and that cuprous oxide could not have been thermodynamically stable relative to these oxides. We also agree that the scenario where dissolution and ex-solution or hydrogen produces a shift in the internal friction peak deserves serious consideration. Either elemental hydrogen or a hydride of magnesium would be capable of causing the shift. We thank Leighly for his well thought out comments. (Baik and Raj 2/22/83)