ABSTRACT

ELECTROCHEMISTRY OF SYSTEMS CONTAINING ALUMINUM PHOSPHATE DISSOLVED IN FUSED BORATE AND PHOSPHATE MIXTURES

by

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The purpose of this investigation was to study the possibility of using, as electrolyte for the deposition of aluminum, systems containing aluminum phosphate dissolved in fused borate and phosphate mixtures.

Aluminum coated metals combine the mechanical properties of the base metal and chemical resistance of aluminum. Electroplating, gives an even and controlled thickness of coating and imparts corrosion resistance.

Methods for the deposition of aluminum previously investigated have not been used commercially, to any extent. Electrodeposition of aluminum was attempted, most frequently from nonaqueous organic solutions and from fused mixtures. Aluminum halides, especially aluminum chloride, was the solutes most frequently used. It is known that aluminum oxide is peptized by aluminum chloride. Severe corrosion is expected on articles electroplated in the presence of aluminum chloride.

In the present investigation, the use of aluminum halides was avoided. Aluminum phosphate was employed in the system $5Na_2O.10Li_2O.6B_2O_3$ as well as in the eutectic mixture of sodium metaphosphate and sodium pyrophosphate. In none of the investigations was an electrodeposit of aluminum obtained.

Investigation of the borates-phosphate mixtures comprised determination of a "fluid range"-composition diagram of the sodium oxide-lithium oxide-boric oxide system. The "fluid range" is a temperature range from an upper value at which, on cooling, liquid becomes viscous, to a lower value at which the solid first appears. These data were plotted on composition diagram which appears as a limiting composition curve and two isothermal, fluid range-composition curves at 600 and at 660 °C. The limiting composition is expressed as the minimum content of the boric oxide which will eliminate all carbon dioxide from the boric acid and alkali carbonates mixture. The area encircled between the 660 °C, upper fluid range and the limiting composition curve is a composition region in which electrodeposition of solid aluminum may be possible. In this region, a mixture of the composition $5Na_2O.10Li_2O.6B_2O_3$ was taken as the solvent for the aluminum phosphate, and the fluid range-composition curve of this mixture was determined. It was found that the addition of aluminum phosphate to the molten $5Na_2O.10Li_2O.6B_2O_3$ has little effect on the fluid range up to 18.68 per cent by weight of aluminum phosphate.

Because the fused electrolyte is very corrosive, its action on different containers was studied. These containers included those made of porcelain, nickel, ampco metal, armco iron, plumbago, graphite and platinum. Except for the graphite and the platinum, no material was suitable for use as a container.

No aluminum was electrodeposited from the molten bath of $5Na_2O.10Li_2O.6B_2O_3$ or from its solution with aluminum phosphate. Both aluminum anode and platinum cathode were covered with black deposits after electrolysis.

The deposits were studided by chemical methods, spectrographical analysis and X-ray analysis. Final results showed that they consisted primarily of carbon. A search for the source of this carbon, formed in the electrodeposition, indicated that it came from the carbon dioxide absorbed from the air by the fused electrolyte. A mechanism for the reaction was proposed.

Electrochemical properties of the electrolyte $5Na_2O.10Li_2O.6B_2O_3$ as well as those of its solution with aluminum phosphate were studied. Both the molten $5Na_2O.10Li_2O.6B_2O_3$ and the molten mixture of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5Na_2O.10Li_2O.6B_2O_3$ showed no decomposition potential on electrolyzing with aluminum anode and platinum cathode. If platinum electrodes were used for borates-phosphate system, the current was constant when stirred, when moisture was added, and when the

electrodes were immersed periodically. The decomposition potential determined for the borates-phosphate system with platinum electrodes was about 1.40 volts, at 600 ± 10 °C. Qualitative electrodeposition tests showed that no aluminum could be deposited from either electrolyte. Quantitative electrodeposition test with the molten $5Na_2O.10Li_2O.6B_2O_3$ showed that the weight loss of the aluminum anode consisted of both electrolytic loss and direct chemical attack.

Also, a eutectic mixture of the sodium metaphosphate and sodium pyrophosphate was used as the solvent to dissolve aluminum phosphate for electrolysis. The molten mixture had a strong oxidizing power, the aluminum anode became passive, and a strong anode effect was observed, if an aluminum anode was used. Black coatings were formed on the copper cathode with either an aluminum anode, or an anode of an alloy of 75 per cent of aluminum and 25 per cent of copper, or a platinum anode. The black coating on the copper cathode was found by chemical analysis to be a copper compound.