AN ELECTROCHEMICAL STUDY ON THE CORROSION AND CORROSION INHIBITION OF Ti, Zr AND Mo.

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AN ELECTROCHEMICAL STUDY ON THE CORROSION AND CORROSION INHIBITION OF Ti,Zr AND Mo

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VITA

Dr. Emad Aboul Seoud Abd El Meguid was born at El Kerateen. Embaba-Giza, Egypt on March 10 th, 1959. He graduated with B.Sc. degree with grade very good, Major Chemistry, in 1981, from Ain Shams University. He was appointed as an assistant researcher in the National Research Centre, Dokki, Cairo.

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The remarkable corrosion-resistance of some metals, e.g., Zirconium, titanium and molybdenum is in favour of safer, wider and more lasting industrial applications of such metals. Diversified and extensive studies have been carried out for the conduct of these metals in different electrolytes and occasions under varying working conditions. Nevertheless, more detailed study seems to be still needed.

The importance of Zr, Ti and Mo and their alloys, is attributed to their ever increasing demands, wide utility and application in many fields of services due to their pronounced corrosion resistance qualifications. So, Zr is used in nuclear reactors as a material having a reasonable transparency to neutrons coupled with moderate strength and good oxidation resistance in high temperature water and in hot carbon dioxide. Titanium is utilized in air crafts and aeroengines as a material of high strength but of low density. On the other hand, Mo has a specialized application as support wires in tungsten - filament lamps and thermionic valves as anode and grid materials, also it is used in missile and aerospace industry.

Zirconium alloyed with small amounts of tin, iron, chromium and nickel (Zircaloy) shows improved resistance to high temperature water. Zirconium and its alloys, in high temperature water, exhibits first a decreasing corrosion rate that may be followed by a rapid linear rate of attack, termed "breakaway" or breakdown".

Numerous elements alloy with tiatnium, commercial alloys include aluminium, chromium, iron, manganese, molybdenum, tin, vanadium and Zirconium. Alloying with 30% Mo greatly increases resistance to hydrochloric acid. Small amounts of tin reduce scaling losses during hot rolling. Small additions of palladium, platinum and other noble metals increase resistance to moderately reducing media.

Molybdenum base alloys are produced for specific application in industrial purposes. For example Mo, 0.5 Ti, 0.8 Zr (designated TZM), Mo,30W and Mo, 30 Ta are manufactured when high resistance is required.

Zirconium and titanium have a very strong affinity for oxygen and their excellent corrosion resistance results from the presence, at the metal surface, of a tenaceous compact film of oxide. Molybdenum has also a good resistance to many electrolytes, however, it has different mechanisms for the oxide formation than the two afore mentioned valve metals, for its complex formation tendency.

The corrosion behaviour of a metal in aqueous media can be correlated with the electrode potential developed between the immersed metal and a reference electrode. Materials which develop a negative potential drift under these conditions will be expected to exhibit little resistance to corrosion by the medium, while those which have a positive potential drift will be corrosion resistant. The electrode potential depends on the conditions of the surface of the metals and can be used, by e.m.f. measurements of this kind, to observe differences and changes in the conditions of a metal surface caused either by various methods of surface preparation or by the action of the solution on these surfaces.

Reaction films may be formed on metals when are put in contact with electrolytic solutions or atmosphere. These films are of great importance for the controlling role they play in determining the reactivity of such metals and are useful as protective and decorative coatings as well as technological devices. Anodic films constitute a special class of reaction films which are produced in electrolytic solutions. Nevertheless, formation from solution permits more freedom in the choice of growth of a reaction film than does formation in gases, specially with regard to the driving force for the reaction. For example, the driving force can be kept the same by holding the potential constant, or can be continuously varied to keep the same role by passing constant current through the cell. Such formations also present some special problems not encountered in gas phase reactions principally with regard to control of composition.

I.1. Zirconium.

Zirconium possesses good corrosion resistance in many environments ranging from highly acidic to highly alkaline aqueous solutions. This is usually ascribed to the presence of a protective oxide film present on the surface, formed either during air exposure or during the initial period of exposure to the aqueous solutions.

Güntherschulze and Betz(1), as early as 1931, studied the kinetics of the formation of anodic oxide films on zirconium among other metals. They applied the analysis of colour and capacity data for films formed in sulphuric acid. Later, they (2) derived the empirical relationship representing the dependence of i, the anodic current density, and H the effective field strength as:

$$i = K \exp BH \quad ....(1)$$

where K and B are constants. Equation (1) describes the high field approximation. Charlesby(3) used surfaces prepared with emery paper under white spirits and made comparison of colour and measured the capacities for different electrolytes. The films formed were stated(3) to be similar in colour and capacity, nevertheless, some differences in thickness were reached which were pointed to be of measuring errors. Films formed in nitric acid were cubic ZrO_2, but those formed in the other electrolytes were mostly amorphous oxide though with trace of cubic ZrO_2(3). The current efficiency was found to be less than 100% and the possible range of thickness calculated to be from 12.5-30 A°/V. Similarity was found (4) between oxide films formed by reaction with air and films formed to the same thickness by anodization. As the current that does not form oxide may be expected to cause oxygen evolution, Charlesby and Polling(5) determined the oxygen evolution and attributed the low current efficiencies obtained to be due to the use of the abraded surfaces.

Below the oxygen evolution potential, oxide will be produced with 100% current efficiency in the absence of any faradaic process such as metal dissolution. This was assumed to be the case$^{(6-11)}$ and at constant current extrapotential, dE across the film is needed for each new layer of oxide, dδ, to maintain the field in the oxide and hence the current, dE/dδ may be called the differential field strength, H_d, and typically does not vary with increasing thickness of oxide at constant ionic current density, however, with some metals it decreases and with others it increases.

The rate of increase of thickness can be given by

$$\frac{d\delta}{dt} = \frac{iM}{nFS} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where δ thickness, t time, i ionic current density, n number of Faradays F required to form the molecular weight of oxide M, and S density. If the differential field strength H_d is constant, the rate of rise of the potential is

$$\frac{dE}{dt} = H_d \frac{d\delta}{dt} = \frac{iH_dM}{nFS} \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

This relation was used to determine H (knowing i) instead of to determine i (knowing H). The expression $(\frac{1}{i})$ $(\frac{dE}{dt})$ was called the "unitary rate" by these authors$^{(6-11)}$and is a measure of H.

The delay of oxygen evolution on zirconium, named as incubation or induction period, is influenced greatly by surface roughness of the metal. Different method of abrasion were discussed(12) to show the effects they produce on the induction period. Chemically polished specimens have zero induction period(13).

The presence of sufficient chloride ions leads(8) to corrosion potentials below that of oxygen evolution, but the potentials was brought above that of oxygen by the addition of nitrate ions in the ratio 5:1 chloride. The peculiar action of nitrate in repairing the film and preventing pitting but the action of chloride correlates with the results of Misch and Ruther(14), who proposed that anodization in nitric acid promotes nucleation of the oxide grains on zirconium. The character(8) of the oxide film structure on the tin alloys which allows a greater permeability to chloride ion than does the oxide film on the pure metal, also renders the fixation of nitrate ion in the film easier and this ion can thus catalyze the formation of additional oxide at the very points where the film is most permeable. Tin, therefore, was deleterious as an alloying element. Chromate, nitrite and phosphate, which are generally good corrosion inhibitors, exhibit a much