CHAPTER - I

INTRODUCTOIN

Almost all metals/alloys undergo corrosion in one or the other environment. This depends upon oxidation power/ionizing capacity of metals and electrochemical power, or aggressiveness of media. In general, corrosion is more significant in acidic media compared to others. On the other hand, high corrosion resistance to wide range of environments is observed in those metals/alloys, which exhibit active-passive transition. Also a minor change in composition of metal/alloy or environment, sometimes dramatically alters their corrosion behavior.

Many metals and their alloys achieve active-passive state in different media and conditions. But the degree of passivation attained will be different in each case. By and large active metals and their alloys quickly attain complete passive state in favorable conditions. Once the passive film has been nucleated on a metal surface, the further growth, nature and behavior of film depends on the chemical, electrical and mechanical properties of the film substance. The most complete passivity is achieved, in general, when the film substance has:

Low ionic conductivity
Appreciable electron conductivity
Very low chemical solubility & dissolution rate.
Stability over a wide range of potential.
Tenacious, well adherent to metal surface and high compression strength.

If metal alone doesn't meet the above requirements fully, suitable alloying addition may improve few or all of these properties. Or increasing the thickness of existing oxide film using anodizing/oxidizing treatment so as to have the above properties.

The excellent corrosion resistance of both, austenitic stainless steel and Titanium relied on their ability to form a stable, continuous and adherent oxide films in presence of air or water. That is, both are exhibiting active-passive behavior in suitable environment, containing oxygen.

Austenitic Stainless Steel is presently considered and have been established as most versatile engineering materials. While Ti and it's alloys were initially developed, in 1950's, for aerospace and allied industries. But now they are being also used in chemical processing and other similar fields. Most of these plants have accepted Ti and it's alloys as a competent candidate, particularly in severely adverse corrosive environment. Important physical and mechanical properties of Ass and Ti are shown below:

ASS	Ti
1. FCC structure	HCP structure
2. No Allotropic form	Allotropic transformation
3. Non-heat treatable	Heat treatable
4. Good high strength	Very good specific strength
5. Non-magnetic	Feebly magnetic
6. With stand high temperatures	Withstand modaratly high Temperatures (~550 °C)

Passivation is attained in both via formation of oxides layer. These films are differing not only in their chemical composition but also in their nature and electrical behaviors. Thus, passivity behavior of ASS and Ti & Ti-Ta can be better understood by nature, composition and quality of these films, formed on metal surfaces. In most aqueous solutions ASS and Ti form films mainly containing oxide of Cr & Ti respectively. But, as indicated by E-pH diagrams, the thermodynamically stable oxides are Cr_2O_3 & TiO_2 respectively, within the stability range of water. Although, Ti and Cr, both are transition elements and form variety of oxides.

As oxides are semiconductors or insulators in their behavior. It is noteworthy that, on one hand, oxides of elements Fe, Cr and Ni present in ASS, are p-type semiconductors(2), where as TiO_2 is n-type and exhibits allotropic forms viz : at low temperature anatase and at high temperatures rutile forms(3). Rutile is crystalline, more closely packed, less tetragonality (a/c=1: 0.6) and denser (4.20 g/cm3) than anatase, which is metastable, microcrystalline with distorted tetragonal structure (a/c = 1:1.8) having density 3.90 gm/cm2 (9% less). Thus anatase is relatively poor semiconductor than rutile, which is also indicated by band gape energy values. For rutile it is 3.0 ev and for anatase is 3.2 ev. Yet other forms of TiO_2 exists which are amorphous or microcrystalline and may or may not act as insulators/ semiconductors. No such allotropy is reported in case of Chromium-oxide. Even with such above mentioned contrast in nature and quality of passive films on ASS and Ti, corrosion is inhibited in both the cases. Therefore, mechanism of this process must be very different and interesting to explore from analogy point of view.

Above aspects were enticing enough to study passivation behavior of these two materials, in different chemical environment. One is already well established, where as for the other, a lot of research has yet to be done to establish it in the field of material. Further, the minor alloying additions like 2-3% Mo in Ass and 5% Ta in Ti may change the passivation behavior, in terms of nature, quality and corrosion resistance of these alloys. Hence in present research work, ASS type 304, Ass type 316, C.P. Ti and Ti - 5% Ta alloys were selected. These materials were readily available in nearby industries. With regards to literature, not much literature is available for corrosion behavior of Ti-5Ta alloy, although a lot of reference are readily available for, SS-304,SS-316(4), C.P.Ti and commercial alloys of Ti viz : T16Al4V, Ti6Al2.33n, Ti.2.0Pd and others[5]. Therefore, this investigation will through some light on corrosion behavior Ti-5Ta alloy, since a lot of similarities in nature and quality of passive films were observed in both these alloys.

Environments used in this work are 5 to 10% HCL, 10 to 20% H_2So_4, H_3Po_4 commercial grade and H_3PO_4 laboratory grade. Considering that these are the most commonly encountered media in the chemical processing units.

Electrochemical measurements conducted are potentiodyne & A.C. impedance techniques using EG & G, M273 system with lock in amplifier. All studies were carried out at room temperature. The results were computed and analyzed using M352 and M398 corrosion software.

Though the general corrosion & pasivation behavior of metals and alloys can be easily understood and established by potentiodynamic studies, the nature, quality & surface characteristic of these passive films cannot be revealed by this techniques. On the other side, Electrochemical Impedance Spectroscopy (EIS) studies also called as AC Impedence technique, used here, can evaluate the nature & quality of film of tiny few microns in terms two components viz. polarization resistance, Rp, and double layer capacitance, Cdl, and provide useful informations.

For characterizing the films formed on surface, SEM studies were carried out for surface topography, where as EDAX and XRD techniques were performed to examine quantitative and qualitative nature of the films in each case. These studies have been used to support potentiodyne and A.C. Impedance results.

Additionally, in case of Ti and Ti-5Ta alloy passivity were developed using simple and economical treatments viz. : Thermal and Electrochemical. All the above treatments mentioned studies were also carried out for thermally treated as well as electrochemically treated Ti & Ti-5Ta specimens to evaluate (nature, quality & capacitance in passivity and its effect in different media) its effects on passivation behavior after increasing the thickness of the passive film.

The thesis consist of total 8 chapters. The details are as under:

The chapter I gives the introduction to the whole thesis. And chapter II and III give the detailed literature on Austenitic Stainless Steel and Titanium and Ti-alloy respectively. These include classifications of these alloys, effect of alloying element. In general, physical, chemical and mechanical properties including applications are given in suitably. The metallurgical factors affecting these alloys in different environments are also discussed in the chapter.

.In chapter IV the experimental detail of potentiodynamic and EIS technique have been explained, which includes equipment used, detail of samples and their preparation, various treatment given and the evaluation procedure. The principles of equipment and plots/format used are also explained in this chapter.

In chapter V and VI, results and discussions on effect of different Austenitic Stainless Steel, Titanium and Ti-Ta alloy in different oxidizing-reducing acidic environments are given in detail. The comparison of results of these alloys in different concentrations of HCl, H_2SO_4 and lab and comm. H_3PO_4 is also done extensively in these chapters. The surface characteristic results obtained for these alloys using SEM and EDAX are also discussed and explained in the chapter.

The effect of oxidizing and anodizing on Ti and Ti-5%Ta alloy are given in chapter VII. The results include potentiodynamic and EIS plots and also surface analysis by SEM & XRD and their interpretation.

In the last chapter VIII an attempt has been made to bring out analogy between ASS with Mo & Titanium alloy with Ta I different acidic media. The analogy between this two passive films stabilized by Mo and Ta respectively in ASS and Ti, is explained by EIS plots and supported by potentiodynamic results along with surface film analysis techniques.

The conclusions and references for chapter V to VIII are given separately at the end of each chapter. This has enabled the author to bring out clearly the effect of alloying elements and environment on these alloys.

At the end of thesis different-annexure are included to provide details and support the discussions.

REFRENCES

(1) Karl Hauffe, "Oxidation of Metals", Plenum Press, p 209, 1965

(2) Karl Hauffe, "Oxidation of Metals", Plenum Press, p 193, 1965

(3) J R Birch and T D Burleigh "Oxides formed on Titanium by Polishing, Etching, Anodizing, or Oxidizing", CORROSION- Vol 56, No 12, p.1233, 2000

(4) Raphl M , Terry Debold and Mark J Johnson ASM Metals Hand Book, Vol 13, Edition 9th, p 550, 1987

(5) Schutz R.W , Growman J S. "Fundamental Corrosion Characterization of High Strength Titanium-Alloys", Industrial Application of Titanium and Zirconium , 4th Vol , STP 917,p. 130-143, ASTM 1986