SUMMARY

The Chapterwise summary of the thesis is presented below:

CHAPTER-I

A comprehensive review of the literature on anodic oxidation of valve metals and fundamental equations for high field ionic conduction have been presented. Güntherschulze and Betz empirical relation, Cabrera-Mott theory emphasizing metal/metal oxide interface control, Dignam's theory of co-operative ions migration through anodic films, Dewald's theory of dual-barrier control, Ikonopisov's theory of electrical breakdown and other related theories have been discussed in view of anodic oxidation of valve metals.

CHAPTER-II

Steady state kinetics data of anodic oxidation of niobium under galvanostatic conditions have been obtained in 0.1N oxalic, citric and tartaric acid over a wide range of temperatures and at different current densities (0.5, 1.5 and 10 mAcm$^{-2}$). The constant $A$ and $B$ of Güntherschulze and Betz empirical relation ($i = A \exp(BE)$) have been found to depend on the nature of electrolyte. The $A$ is temperature dependent while $B$ is temperature independent. Dignam's approach which explained the field and also anomalous
temperature dependence of Tafel slope (\( \frac{\partial E}{\partial \ln i} \)) have been attempted. Steady state oxidation data are reported by three parameters (i) pre-exponential factor, (ii) a Morse function distance parameter and (iii) the activation energy. Therefore, Dignam's approach though able to explain the temperature independent behaviour of Tafel slope, but still it could not be applied to our data as various parameters (\( \mu^*, \omega^*, \phi, \gamma, i_o \) etc.) varies with temperature and current density. Hence, any single barrier theory is not able to explain our data and this may be due to the existence of the space charge within the film.

CHAPTER-III

In obtaining steady state kinetics data by procedure outlined in Chapter-II, it is experienced that it is difficult to obtained specimens having identical surface conditions and due to this difference the anodization rate and current efficiency are affected. Hence, in this Chapter, a refined technique is employed for anodic growth of oxide film on niobium which gave very satisfactory results and difference in specimens with regard to their surface is completely eliminated. Ionic conduction at high field strength on niobium is studied in 0.1N oxalic acid at various temperatures (0-61°C) and at different current density sets (0.2-2, 0.4-4, 0.6-6, 0.8-8, 1-10 mAcm\(^{-2}\)). Tafel slope is again found to be temperature independent.
Dewald's double barrier control theory which takes into account the space charge effect has been examined in this Chapter and using this theory various parameters of anodic oxidation have been evaluated.

The entrance barrier energy has been found greater than the corresponding diffusion barrier energy when ratio of the half jump distances of the diffusion barrier to that of entrance barrier \((a/b)\) is less than unity. This suggests that the rate controlling step is at metal/metal oxide interface. But the entrance barrier energy is of the same order that of diffusion barrier energy when the jump distances ratio is more than one. Therefore, the rate controlling step in the kinetics of growth of anodic oxide film is not only at the metal/metal oxide interface but also across the film. The contribution of space charge has been obtained during the growth of the anodic oxide film on niobium and it increases with increase of temperature. Therefore, our data could be explained satisfactorily by Dewald's theory if \(a/b\) is greater than one.

**CHAPTER-IV**

In this Chapter a systematic study of electrical breakdown on \(\text{Nb}_2\text{O}_5\) films as a function of temperature, concentration and composition of electrolyte and current density has been made. Electronic current
measurements through the oxide film as a function of temperature and applied field are also carried out. The criteria for observing the breakdown voltage \( U_B \) is the evolution of gas at oxide film surface which makes the applied voltage static for sometime (say 100 seconds). The Ikonopisov's theory of electrical breakdown has been examined critically.

It has been found that breakdown voltage depends upon the concentration, composition and temperature of contacting electrolyte and current density employed for anodization. The Ikonopisov's theory of electrical breakdown provides a theoretical justification to the effect of temperature, concentration, composition and applied field on \( U_B \). It has also been found that electronic current \( j_e \) decreases with increase in temperature and applied field. Higher value of \( U_B \) at a particular concentration for citric and tartaric acid electrolyte than oxalic acid suggests that concentration of citrate and tartarate ions incorporated is less than that of oxalate ions.

**CHAPTER-V**

In this Chapter rectification characteristics of \( \text{Nb}_2\text{O}_5 \) films of various thicknesses with vacuum deposited metals (Al, Ag, Bi and Sn) contacts have been made. Electrical conduction through these oxide films as a function of field strength, temperature and thickness have been
measured. In all these systems the conduction is asymmetric and there does not appear to be any correlation between critical voltage and work function or work function difference for these metal electrodes. Dominant carrier transport in these systems is through Schottky conduction mechanism. The same conduction mechanism is operative irrespective of the polarity of the metal electrode.

CHAPTER-VI

This Chapter deals with the properties and other aspects of the anodic oxide films on niobium. These are given below:

i) **Ion Mobility Studies:** Mechanism of ion transport through anodic oxide films on niobium employing Sandwitch experiments have been studied. These show that only metal ions are mobile during the growth of anodic oxide film on niobium in aqueous electrolytes.

ii) **Current Efficiency:** Current efficiency is determined by weight gain method. At lower concentrations of electrolyte (0.01, 1 N), current efficiency is found to be unity. But for higher concentrations of electrolyte (10, 14.95 N), current efficiency is more than unity. It has been found that the experimental mass gain of niobium specimen (due to oxygen uptake) during anodization is greater than that expected for the formation of Nb$_2$O$_5$ film in higher concentration of electrolyte. This shows that the mass
gain is probably due to the incorporation of ions into the oxide films.

iii) Dielectric Measurements: Effect of temperature, time and current density on dielectric properties have been studied. It has been found that capacitance increases with increase in temperature and does not affected with time. But it decreases with increase in current density. Loss factor (\( \tan \delta \)) also decreases with increase in current density and temperature.

iv) Effect of Halide Ions: Addition of chloride ions increase the capacitance of \( \text{Nb}_2\text{O}_5 \) film slightly. This suggests the little corrosion action of chloride ions on \( \text{Nb}_2\text{O}_5 \) film. Same type of effect is also observed when anodic oxide films on niobium are formed in various concentrations of sulphuric acid electrolyte.

v) Heat Treatment of \( \text{Nb}_2\text{O}_5 \) Films: Heat treatment of the oxide films in air makes these more conducting. This effect depends on the time and temperature. Capacitance of \( \text{Nb}_2\text{O}_5 \) film increases on annealing.

vi) Formation Characteristics and Breakdown Phenomenon in the Presence of UV Radiations: The data obtained during the growth of anodic oxide films on niobium show that rate of growth decreases in presence of UV radiations. This is due to the development of positive space charge near the solution/oxide interface which increases the electronic
current in the film. The increase of breakdown voltage value in presence of U.V. radiations may be due to decrease of recombination constant (r) and increase of impact ionization constant ($\sigma_m$).