A Critical Analysis of Mott-Cabrera's Equation in the Study of Low Temperature Oxidation of Copper and Its Alloys

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A detailed investigation on low temperature oxidation behaviour of copper and its alloys in the thin film range has been carried out. The reciprocal logarithmic law of oxidation formulated by Mott-Cabrera has been found to be valid. To test the validity of this rate law, a new approach has been made through the assumption of prohibitive activation energy idea. The technique has enabled to fit the experimental data better for both rising and limiting part of the rate curve, thereby eliminating the drawbacks of the graphical integration method. A quantitative relation has been proposed for the concept of prohibitive activation energy idea and its validity has been well eatablished. Quantitatitive estimation of the different parameters of the Mott-Cabrera equation has been performed and found to be in good agreement with that reported in literature. The effect of small amount of chromium as an alloying element has been found to enhance the rate as well as the limiting thickness. The element lithium has shown the reverse effect. The experimental evidences completely put to rest the doubts raised by Grimley and Trapnell, Hauffe *et al.* regarding the variation of potential across the reaction interfaces. The importance of incorporation reaction at the outer interface has been suggested to be the guiding factor in fixing the magnitude of resultant potentail.

THE controversy of the picture in the fleld of thin film formation on metals can be solved by a precise evaluation of the physical characteristics of some metal-oxygen systems. Important parameters relating to metal oxidation are: (a) the extent and structure of metal surface (b) the physical and compositional non-uniformity of the oxide film, (c) proper considerations for the boundry conditions imposed on the range of film thickness, (d) experimental temperature range, and (e) partial pressure of the gas which is reacting with the bare metal surface.

A low temperature oxidation study of copper and its alloys is a promising system from this point of view. The thin oxide films formed on pure copper at low temperatures are physically and chemically homogeneous; moreover there exists considerable information on the semiconductor properties of its oxides[1]. In addition, the structure and orientation characteristic[2] of cuprous oxide films formed at low temperatures have been thoroughly investigated. The pioneering work on low temperature oxidation of copper by Rhodin [15,16] Lustman and Mehl[17], Allen[18], Miley and Evans[19], Young et al[2], Krishnamoorthy and Sircar[20,21,22,23] provided ample evidence to the fact that at low temperatures oxidation occurs rapidly but practically ceases in a relatively short time forming highly stable oxide films of a few angstroms thickness. Such a situation was common to many a metal and was thoroughly studied for the first time by Mott[3,4] and his associates[5,6], which led to the formulation of new ideas on the mechanism of thin film formation at low temperatures. Towards the end of forties, Mott and Cabrera[3] came out with the idea that when the film is very thin, the electrical potential gradient that is set up across a growing film will have very high magnitude (of the order of 10^6–10^7 V/cm) and under such potential gradient the migrating species will feel the pull for migration even though the thermal energy is not sufficient to activate them. They theoretically derived rate equations for film growth basing on adsorption of oxygen on the oxide surface and its ionisation by capture of electrons from the metal by electron tunneling or thermoionic emission. At low temperatures the ions could not simply diffuse through the film due to a concentration gradient; rather the electrons could easily migrate from the metal to the oxygen adsorbed on the surface of the film resulting creation of cations at the metal/oxide interface and oxygen anions at the oxide/oxygen interface.

Later on, Hauffe[7] and others [8,9,10,11] have criticised Mott-Cabrera's hypothesis on two fundamental assumptions which were not explicity stated in their theoretical derivation. Firstly in Mott-Cabrera's derivation, space charge effects were not accounted for which may be neglected for films thicker than a few hundred angstroms. Secondly, Mott-Cabrrra's theory assumed that the defect concentration within the thin oxide layer to be constant which is not true because the reactions at the

two phase boundaries were assumed to be very fast and it is the transport through the reaction product which determines the rate of the total process. Under such circumstances, unchanging lattice defect concentrations are produced at the two phase boundaries which can have values of different order of magnitude leading to a strong concentration gradient.

However, Hauffe and Ilschner[12] have shown that the same rate equations can be derived without making these assumptions and concluded that in the very thin film range of oxidation Mott's assumptions are valid. They considered that both electron tunneling and ion migration could be rate determining during different portions of oxide growth.

Fromhold and Cook[13] have just reversed the idea of Hauffe and Ilschner. They proposed that the oxide growth is initially controlled by ion migration followed by electronic tunneling current.

In a recent publication Mott and Fehlner[14] have critically reviewed the different theoretical ideas on low temperature oxidation of metal put forward by different groups of researchers and tried to correlate them to the experimentally observed facts wherein they commented that only through further experimental results, an unified theory on low temperature oxidation could be worked out.

In an earlier work[24] on low temperature oxidation of copper from this laboratory an attempt was made to analyse the experimental date using the differential form of Mott-Cabrera's equation, thereby eliminating all the boundary conditions imposed and the assumptions made which were not universally valid. The method used by Krishnamoorthy et al[24] was a graphical integrations technique where the maximum emphasis was on the rising part of the rate curve. But when it was applied to fit the data of the limiting part in the rate curve, it did show a low but appreciable rate of growth beyond the limiting time. The present technique of examining the validity of Mott-Cabrera's equation for thin film formation on copper and its alloys is based on consideration of the limiting thickness value and concept of limiting field with an assumption regarding the value of W, which previous authors[24] proposed to be equal to 1 e. v. at 30°C when a limiting thickness of 44 Å is reached for copper.

EXPERIMENTAL

Spectrographic analysis of the copper used showed the following composition.

Ni = 0.23%, Ag < 0.003%, Bi = traces and rest copper. The alloys used had the following composition :

(a) Cr = 0.03% and rest copper.

(b) Li = 0.3% and rest copper.

The specimens were used in the form of thin sheets measuring 2.5 cm long, 1 cm wide and 0.05 cm thick. The method of sample preparation and their surface preparation were the same as those discussed in the author's previous works[21,22,23]. The experimental details for oxidising the samples at different temperatures of 5°, 30° and 45°C and the method of film thickness measurement have already been discussed earlier[24].

RESULTS AND DISCUSSION

The results pertaining to the oxidation behaviour at the three different experimental temperatures for copper, copper-chromium and copper-lithium systems are presented in Figs. 1, 2 and 3 respectively. It has also been established that the thickness of the oxide scales developed on copper containing small amount of nickel and silver were identical to that of high purity copper (99.999%). Since the results of the low temperature oxidation study have been analysed on the basis of Mott-Cabrera theory of growth of very thin oxide films, their equation used in the present analysis together with the nomenclature can be presented as :

$$\frac{dx}{dt} = K' \exp (X_1/X) \qquad (1)$$

where, $K' = N\Omega\nu \exp(-w/kT)$

$X_1 = \frac{1}{2}(qaV/kT)$

and X = thickness at time, t.

Hence, $\frac{dx}{dt}$ = rate of oxidation at thickness X(Å/hour),

N = number of mobile species available/cm²,

Ω = volume of oxide formed/metal ion in cm³,

ν = frequency factor = 10^{12}/sec

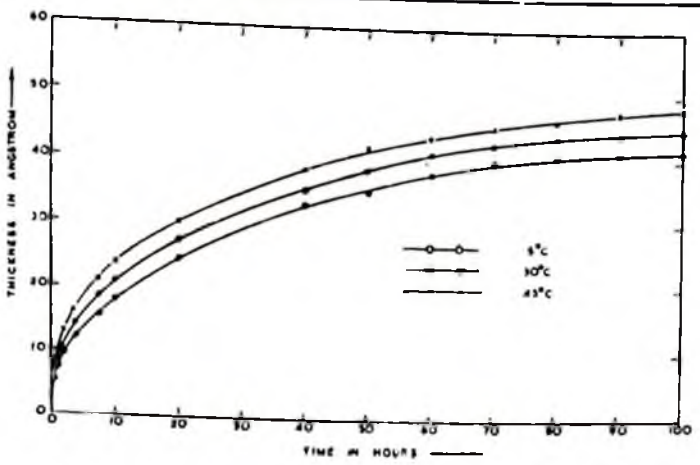


FIG. 1 THICKNESS – TIME PLOT FOR PURE COPPER AT 5°C, 30°C AND 45°C

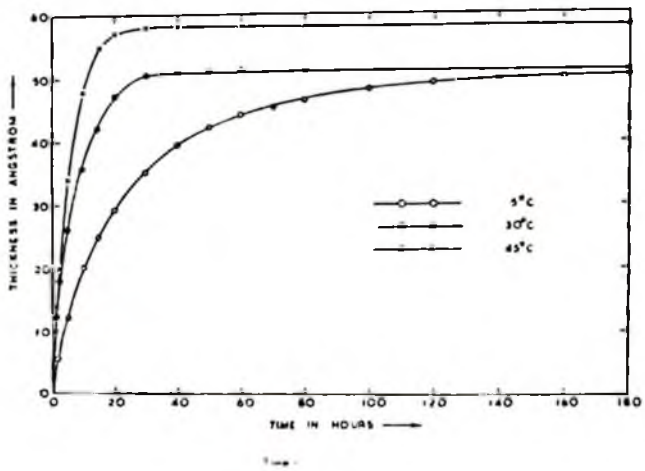


FIG 2 THICKNESS – TIME PLOT FOR COPPER – CHROMIUM ALLOY AT 5°C, 30°C AND 45°C

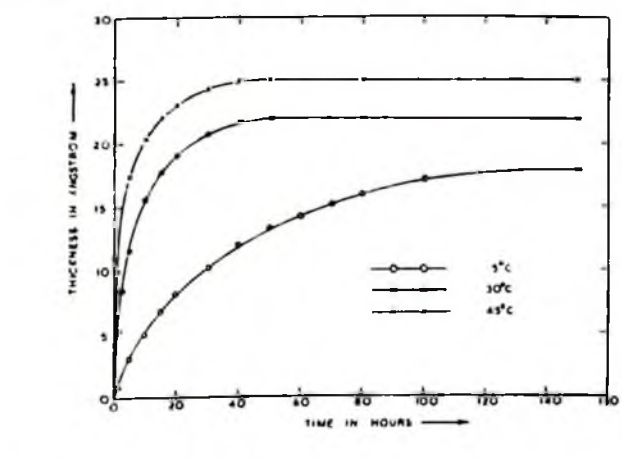


FIG 3 THICKNESS – TIME PLOT FOR COPPER – LITHIUM ALLOY AT 5°C, 30°C AND 45°C

W = sum of energy of solution of a metal ion in the oxide (W_i) and the activation energy for the ion to transit from one interstitial position to the next (U) in e.V.

k = Boltzmann constant = 1.38×10^{-23} Joules/°K,

q = electronic charge = 1.6×10^{-19} coulombs,

a = lattice constant of the oxide (cation-cation distance)

= 4 Å for Cu_2O,

V = potential difference between the metal/oxide and the oxide/gas interface in volts,

and $\frac{V}{X}$ = field strength under which the mobile species migrate.

Taking logarithms on both sides of equations 1,

$$\log\left(\frac{dx}{dt}\right) = \log K' + \left(\frac{X_i}{.303\,X}\right) \qquad (2)$$

Hence according to equation (2), the plot of log $\left(\frac{dx}{dt}\right)$ vs 1/X should yield straight line provided K' and X_i are independent of X and the intercept, which the line makes on the log (dx/dt) axis = log K' = log $(N\Omega\nu) - (W/2.303\ kT)$ and slope $= \left(\frac{X_i}{2.303}\right) = \left(\frac{q.a.V.}{2 \times 2.303\ kT}\right)$.

Accordingly for judging the validity of Mott's equation under the present experimental conditions, the slope values (dx/dt) have been measured at different X values from the X-t plots and the computed log (dx/dt) values are plotted against 1/X for all the three systems as shown in Fig. 4, 5, 6 respectively, which are found to bear a straight line relationship in agreement with Mott-Cabrera's inverse logarithmic equation. The three straight lines corresponding to three different temperatures of experimentation for each system were found to be parallel to each other. The intercepts on the (dx/dt) axis and the slope values corresponding to the three different temperature lines for all the three systems are computed and tabulated in Tables 1, 2 and 3 respectively. Since X_i involves a kT term in eq (2) the parallelism of the three lines clearly indicate that V must be changing with temperature though the variation may not be of very high magnitude.

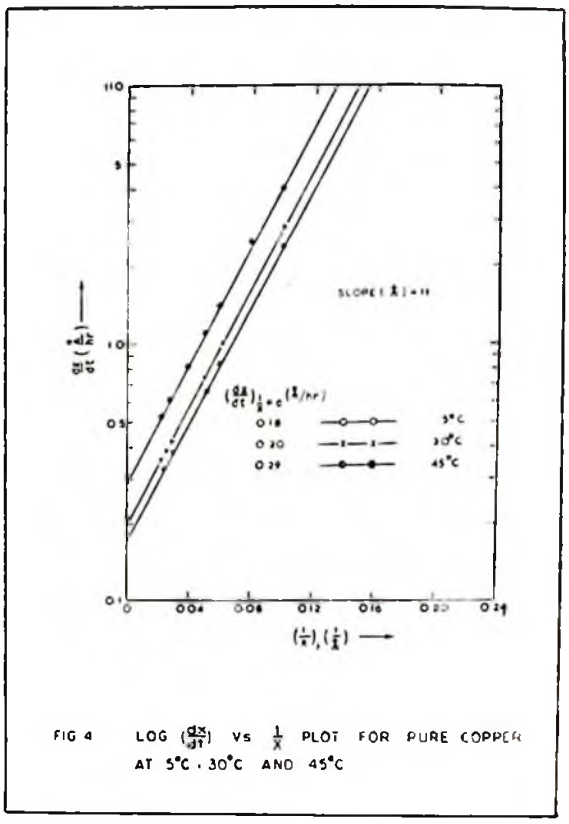


FIG 4 LOG $(\frac{dx}{dt})$ Vs $\frac{1}{X}$ PLOT FOR PURE COPPER AT 5°C, 30°C AND 45°C

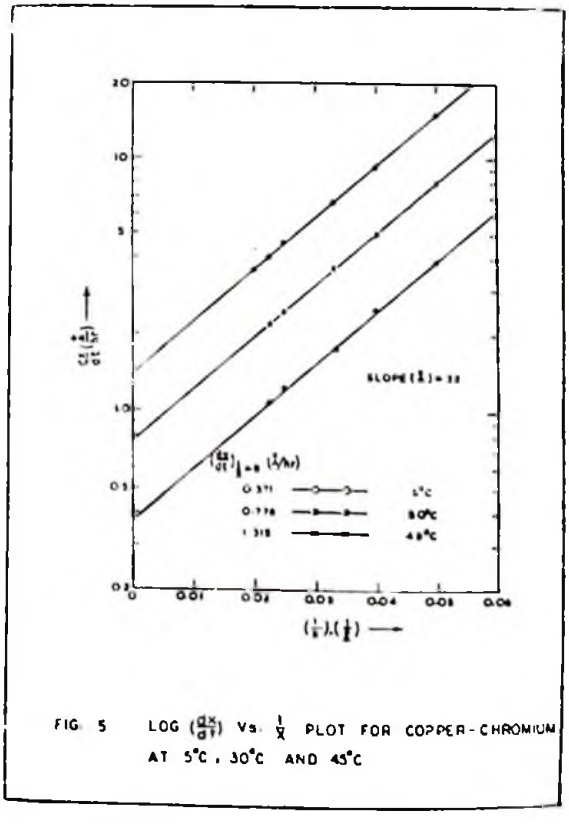


FIG 5 LOG $(\frac{dx}{dt})$ Vs $\frac{1}{X}$ PLOT FOR COPPER-CHROMIUM AT 5°C, 30°C AND 45°C

Now, from the slope values (X_i/2.303), values of V have been computed for different temperatures

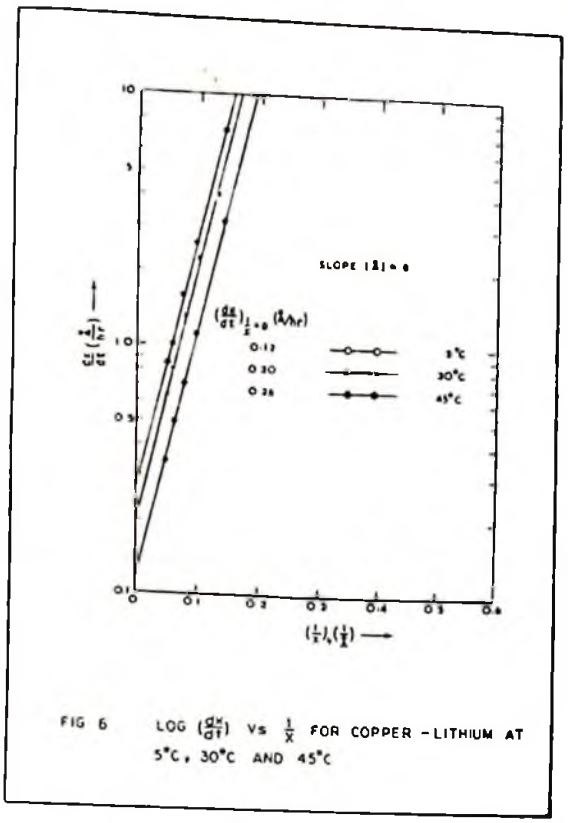


FIG 6 LOG $(\frac{dx}{dt})$ Vs $\frac{1}{x}$ FOR COPPER – LITHIUM AT 5°C, 30°C AND 45°C

by substituting proper values of quantities like q, a and k as shown in Tables 1, 2 and 3.

It is to be realised that Mott-Cabrera's equation fundamentally comprises of two unique components the first one consisting of terms like N, Ω, ν, which are considered to be the frequency part of the generalised kinetic equation and the second one is the exponential part representing the driving force for the reaction. The equation distinctly shows a part where the rate goes on changing and in this region, the energy term can be automatically taken to be independent of temperature. This energy component of Mott-Cabrera's equation comprises of two opposing energy values, the inherent energy barrier height and the field assisted energy term which cuts down the inherent energy barrier. Mott and Cabrera envisaged that all systems obeying this equation during their course of oxidation should reach a limiting thickness value. At the limiting thickness, the field assisted energy value fails to lower the inherent activation barrier to a value such that the reaction cannot proceed further. This is because the magnitude of the field (V/X) decreases as X goes on increasing. At the limiting point, the exponential terms should therefore reach a value of activation which cannot be surmounted by the reactants. So automatically this energy value will be lower than that of inherent energy barrier height.

TABLE I

Slopes and intercept values with other parameters of the Mott-Cabrera's equation at three different temperaturers for copper

Temp. (K°)	Slope $\left(\frac{X}{2.303}\right)$	Intercept. K'(A/hr)	B(eVA) = X kT	X_L (A)	V (voltage)	N No./cm³)	W (ev)
278	11	0.18	0.622	41	0.300	1.40×10^{15}	0.92
303	11	0.20	0.672	44	0.325	$1.70 \times 1-^{15}$	1.10
318	11	0.29	0.712	47	0.345	2.25×10^{15}	1.05

TABLE 2

Slope and intercept values with other parameters of the Mott-Cabrera's equation for copper-chromium systems at three different temperatures

Temp. (K°)	Slope $\left(\frac{X}{2.303}\right)$	Intercept. K'(A/hr)	B(eVA) = X kT	X_L (A)	V (volts)	N No./cm³)	W (ev)
278	22	0.371	1.22	50	0.60	2.52×10^{15}	0.930
303	22	0.776	1.32	52	0.65	5.00×10^{15}	1.009
318	22	1.318	1.40	58	0.69	8.90×10^{15}	1.060

TABLE 3

Slope and intercept values with other parameters of the Mott-Cabrera's equation for copper-lithium system at three different temperatures

Temp. (K°)	Slope $\left(\frac{X}{2.303}\right)$	Intercept. K (Å/hr)	B(eVÅ) = X kT	X_L (Å)	V (volts)	N No./cm²	W (ev)
278	8	0.15	0.434	18	0.217	0.12×10^{15}	0.993
303	8	0.20	0.470	22	0.235	0.68×10^{15}	1.006
318	8	0.26	0.498	25	0.249	1.28×10^{15}	1.056

The rising part of the rate curve was thoroughly examined in this laboratory to establish the validity of Mott-Cabrera equation for low temperature oxidation of copper[14]. But very close to the limiting thickness, deviations were observed, as a result of which log (dx/dt) values had been plotted only till the beginning of nose of the rate curve. It was also observed that different limiting thickness values were reached at different temperatures as well as with addition of alloying elements. On analysing the limit part, it is inferred that the activation energy part should have a constant value at all temperatures obeying the inverse logathimic equation, above which the reaction cannot proceed further at an appreciable rate. This energy value was calculated from the relation of $\left(W - \frac{B}{X_L}\right)/kT$, assuming W = 1.00 e.v. at 30°C, when the corresponding limiting thickness value of 44Å is reached and $B = X_L kT$ from eq (1). This limiting activation energy value at 30°C was equated to calculate the different values of W for different limiting thicknesses at different temperatures as presented in Tables 1, 2 and 3 respectively.

Now, for a known value of (dx/dt) at a chosen X value the thickness-time curve corresponding to a particular temperature, value of N has been calculated from eq (1) considering $\nu = 10^{12}$/sec and $\Omega = M/2\rho N^*$, where M = molecular weight of the oxide = 143 gm, ρ = density of the oxide = 6 gm/cc, N^* = Avogadro's number = 6.02×10^{23}.

The variation in the values of N with temperature and alloying additions are shown in Tables 1, 2 and 3 respectively.

On investigating the dependence of oxidation rate for copper, copper-chromium and copper-lithium alloys on the temperature of oxidation in the thin film range it is clearly observed that with increase of temperature, the rate of oxidation at any particular instance and the limiting thickness goes on increasing. The higher rate of growth with increasing temperature may be due to contribution from either $N\Omega\nu$ term or $e^{-W/kT}$ term or $\frac{qaV}{2\,kT}$ term or it might be a conjugal effect of all the three terms as conceived from Mott-Cabrera equation[3]. From the slope values of the plots log (dx/dt) vs (1/X), it is apparent that $\frac{qaV}{2\,kT}$ has a constant value for all the three temperatures. So in the rising part of the rate curve for any value of oxide thickness (X), the rates should not have changed if $\frac{qaV}{2\,kT}$ was at all responsible for the difference in the rate as observed for the three different temperatures. Therefore, the change in the growth rate must have been contributed either by $N\Omega\nu$ term or $e^{-W/kT}$ term or both of them simultaneously.

As per values shown in Tables 1, 2 and 3 it is clear that both N and W are dependent on temperature. The W term has been found to increase with temperature, whereby the value of $e^{-W/kT}$ goes on decreasing with temperature. Considering the values of Ω and ν to remain unaffected, values of N have been found to increase with increasing temperature. Automatically the rising part of the curve is acted upon by two diametrically opposite factors arising out of temperature. This partly explains the reason behind observance of different rates for the different temperatures at any fixed value of thickness (X). If the situation would have been such that both exponential and pre-exponential terms would have changed in the same direction with the variation of temperature, the growth rate curves would have been symmetrically shifted towards higher rate values with the increase of temperatature. But in actual practice they do not resemble so.

The most interesting feature of the rate curves is that, the limiting thickness values have also been found to increase with temperature. The genesis of the limiting concept was incorporated in the driving force factor or activation energy factor by Mott-Cabrera[5] in their original equation. This activation energy part consists of inherent activation barrier height (W) and field assisted lowering of barrier height (B/X_L). In any oxidation process obeying Mott-Cabrera's theory of thin film formation, there shall always be an activation barrier comprising of these two terms, above which value, energitically, the process becomes prohibitive so that the reaction does not proceed at an appreciable rate. Such a situation is expected when X is greater than X_L (limiting thickness). But so long as X is less than X_L, B/X_L factor is large enough to cut down the activation barrier, and when $X = X_L$, the activation barrier reaches the prohibitive value leading to ceasation of the process of reaction. Since W/kT value goes on increasing with decreasing temperature, and X_L value remains constant, the difference increases leading to a limiting thickness of lower value with decreasing temperature and the prohibitive activation barrier is reached earlier with lower limiting thickness (X_L) value.

The studies on Cu-Li and Cu-Cr alloys in the same temperature range also showed similar trends in the rising part and limiting part of the rate curves with the variation of temperature as is observed for unalloeyd copper. But so far as the comparative value of rate or limiting thickness is concerned for the same temperature of experimentation, there is qualitative difference between the alloy systems themselves as well as with that of unalloyed copper. With the addition of lithium and assuming that most of it goes into solution at room temperature in the alloy, both the rate and the limiting thickness values have fallen drastically. With the incorporation of chromium, these values have gone up appreciably. The rise or fall in the rate values is reflected in changes that have taken place in the values of N and W. The value of N_{Cu} at 30°C $= 1.7 \times 10^{15}$ No./cm^2 in comparison to the value of $N_{Cu-Li} = 0.68 \times 10^{15}$ No./cm^2 and $N_{Cu-Cr} = 5.00 \times 10^{15}$ No./cm^2. Similarly the value of $W_{Cu} = 1.00$ eV. instead of $W_{Cu-Li} = 1.006$ eV. and $W_{Cu-Cr} = 1.009$ eV. at 30°C. This clearly shows that W value has not changed appreciably ; in other words, whether the rate is enhanced or retarded depends mostly on the value of N, which is nothing but the number of mobile species per unit surface area to cross the barrier. Perhaps, the migration mechanism at low temperatures is based on vacancy migration principle which makes the concentration of mobile species approximately equal to the concentration of vacancies as predicted by Mott-and the calculated values are in good agreement with that obtained by Wagner[26] for Cu_2O. It is already known that Cu_2O is a metal-deficit type (p-type) semiconductor with vacant copper lattice sites. Now if a cation of lower valency like lithium ion, which is more electronegative than the solvent metal is added to it, and if the oxide of the solute is soluble in the oxide of the solvent, then these lithium ions will occupy the vacant sites of the base oxide thereby putting resistance to the normal outward migration process. If excess of lithium is incorporated into the alloy, then it might even replace some of the copper ions from the normal lattice position and in doing so during the course of oxidation, the vacancy concentration of the oxide as a whole should decrease. The value of N in lithiated copper confirms the above proposed mechanism. If trivalent chromium ions are introduced in the normal lattice sites of Cu_2O, then it will try either to replace copper ions from the lattice site and thus create new cation defects while the number of electron defects decreases or enters the vacancies. For every chromium ion entering a vacancy or replacing copper ion, to maintain electrical neutrality in the oxide, additional vacancy has to be formed or hole has to be annihilated. So the incorporation of chromium ions will ultimately result in murtiplication of the number of vacancies resulting an increased oxidation rate which is evident from the experimental results. Calculations have also confirmed the increased value of N for Cu-Cr system than that of copper. The fact that the vacancy concentration changes with the addition of chromium or lithium and therby changes the concentration of mobile species in a direction similar to that of vacancy change perhaps indicates a mechanism where the rate-controlling step is expected to be the migration of vacancy and identifies vacancies as the migrating species of Mott-Cabrera equation.

The limiting thickness values of the three systems are found to be copper = 44 Å, copper-lithium = 22 Å and copper-chromium = 52 Å at 30°C and correspondingly X_I values are 25 Å, 18 Å and 50 Å respectively. Since the values of W are not much different for the three systems, the field assisted reduction of activation value $\left(W/kT - \frac{X_I}{X_L}\right)$ will be dependent on the value of (X_I/X_L) so as to reach the energy level for prohibiting the course of reaction. It means that when X_I is higher, X_L has to be higher and this is the case for Cu-Cr alloy where X_I has the highest value, so to reach the prohibitive value of activation energy. X_L has to be the highest, This argument also holds good for Cu-Li alloy showing the lowest limiting thickness value.

Mott and Cabrera [5] suggested qualitative estimate of the growth rate to be equal to 10^{-13}cm in 10^5 sec when the limiting thickness is reached. In the present study calculated value of rate from the estimated quantities in Mott-Cabrera equation has been found to be in good agreement to that suggested by them. The above analysis explains the nature of variation in rate and limiting thickness values attained for the different systems in a qualitative way. Neverthless, it can be emphasised that the analysis has self consistency. But till now no attempt has been made to explain the nature of variarions that have been observed in the values of W, N and V and to provide evidence in favour of the idea of utilising prohibitive activation energy on a general way for tarnishing reactions in the thin film range obeying Mott-Cabrera's theory.

In the present study, it is assumed that the prohibitive activation value to be constant for a particular metal-oxygen system at a particular temperature, denoted by A, which is equal to $\left(W/kT - \frac{X_I}{X_L}\right)$, where W, X_I, k, T and X_L bear the usual signficance.

$$\therefore \quad A = W/kT - \frac{X_I}{X_L}$$

$$\text{or,} \quad X_L = \frac{X_I}{(W/kT - A)}$$

If the above assumption is presumed to be correct, then X_L vs $\frac{X_I}{(W/kT - A)}$ should yield a linear plot for all the systems studied in the present investigation along with the results of the previous study reported[20,22] on this context and oxidation in presence of moisture[25] which is being communicated for publication shortly. The results are g aphically presented in Fig. 7 which shows that the plot represents a good linearity with slope of proper magnitude well within the limits of errors. This clearly proves the perfection of our concept of prohibitive activation barrier to explain the low tempetature oxidation characteristics of the copper oxygen system in the thin film range.

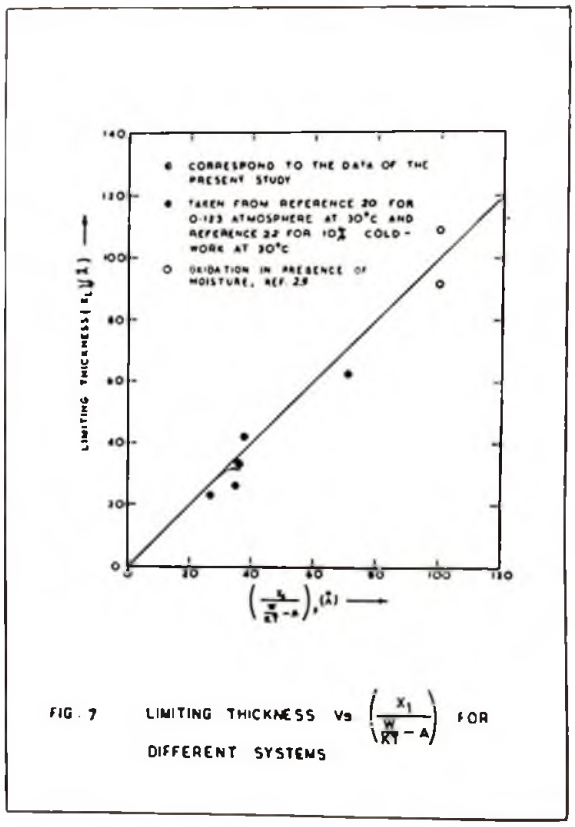


FIG. 7 LIMITING THICKNESS Vs $\left(\frac{X_I}{W/kT - A}\right)$ FOR DIFFERENT SYSTEMS

The absolute values of V i.e. the potential that is developed across the two reacting interfaces have been found to be of the same order as reported by Mott[5]. The value of potential as estimated in this study has been found to depend on temperature and alloying constituents. It has been found to increase with temperature for all the three systems. The most interesting feature is that changes in the value of V is accompanied by a change in the concentration of defects which indicate that the concentration of defects has some bearing on the potential that is developed across the reacting interfaces. If mobile species are assumed to be represented by vacancies as already

found justifiable in the case of Cu-Cr and Cu-Li systems, a possible mechanism for the variation in V can be ascribed. It is assumed that at the outer interface an equilibrium is established between the ionised oxyzen atoms or molecules and the lattice cations giving rise to metal oxide with vacancy as represented :

$$O^{-}_{ads} = (Cu^{+}\square/X) + Cu_2O,$$

where, $Cu^{+}\square/X$ is the concentration of vacant cationic site.

Now, on increasing the concentration of vacancy, the equilibrium of the reaction will get shifted to the left, thereby increasing the field creating oxyzen ions which will ultimately give rise to a higher V value. This adequately explains the change in the value of V with the variation in the defect concentration.

The magnitude of change in the value of W for different conditions of experimentation was found to be very small. With such small change as encounered in the present calculations, it is rather difficult to conclude anything specially relating to its effect on the course. of reaction. Moreover, the W term embodies two energy terms and as such its variation can be attributed to either of them or both in a conjugal way. $W = W_i + U$, where, W_i = heat of solution for a positive ion and U represents the activation energy for migration of diffusion.

All the experimental evidences that have been put forward, overwhelmingly support the role of defect concentration predominently affecting the rate process. Therefore, it is felt that perhaps the energy of transit term contributes more towards the total inherent energy barrier than the energy of solution term. Normally, with the introduction of more and more vacancies, one would expect the diffusion process to be eased, resulting a decrease in the W term but the present experimental evidences do not provide enough information regarding such variation of W. It is not certain that the energy of solution term has increased more than the decrease in the energy of transport term leading to a higher W term with increase of tsmperature or with the incorporation of chromium ions. Of course, the magnitude of change observed under different conditions of experimentation does not warrent a conclusive decision.

According to Grimley and Trapnell[27] the mobile species as represented in Mott-Cabrera equation should designate the number of adsorbed ionised oxygen atoms on the surface of the oxide and that for all conditions of oxygen pressure more than a few mm of Hg, the su face charge due to ionised oxygen atoms or molecules is constant giving rise to a constant potential (V). Under such circumstance, the estimated values of N should have shown a direct relation with V, because the potential that is developed between the two reacting interfaces is something of the type of a capacitor. But in actual practice, the N vs V plot did not show such trend. Therefore, Grimley's idea of identifying the mobile species as surface absorbed ions or atoms can be ruled out. Further, the noticeable change in the rate of tarnishing under externally applied electric current as reported by Krishnamoorthy et al[21] also seems to contradict the assumptions of Grimley and Trapnell[27].

The previous reporting[22] on the effect of cold work on the kinetics of oxidation of copper has further supplemented to an understanding of the mechanism of the process, whereby it was found that with a decrease in vacancy concentration, the rate of tarnishing decreased. The effect of change in vacancy concentration brought about either at the metal/oxide interface (by cold working[22]) or at the oxide/gas interface (by change of partial pressure[20]) or in the bulk oxid (by Li or Cr incorporation[23,24]) have been found to affect the rate of tarnishing appreciably. Perhaps, this indicates that the vacancies are more or less uniformly distributed irrespective of its source of generation. Mott and Cabrera did not consider any contribution to the rate from the contribution gradient, but assumed the concentration of defects to be uniform throughout the film. Therefore, the primary rate-determining step may be a direct function of the vacancy, which, in turn may be, either due to movement of cations from the surface layer of the metal in the oxide to the nearest available vacancy or due to the movement of vacancy towards the reacting interface. So, when the available vacancies are smaller in number, the probability for a cation to jump through the kink will be restricted as the number of nearest available vacancies are less, leading to a decrease in the oxidation rate. Once the ions have crossed the inherent energy barrier, they will be dragged to the other reaction interface by the pull of the field.

CONCLUSIONS

1. Previous studies from this laboratory established the validity of Mott-Cabrera's reciprocal logarithmic law for tarnishing of copper at and around room temperature through graphical evaluation method which was not adequate in explaining the limiting thickness value and rate. The test of validity used in the present study is different from that of others. From the limiting thickness value of the rate curve, other parameters of the Mott-Cabrera equation have been calculated utilising the concept of prohibitive activation barrier and the experimental data have been found to fit the calculated values within reasonable limits of errors in the experimentation.

2. The effect of chromium and lithium addition to copper in order to change the defect concentration of the oxide have provided sufficient information to believe that the bulk defect concentration affects the growth rate in a marked way.

3. Mott Cabrera's assumption of constant potential difference between the two reacting interfaces and the prevalence of variable field strength have been amply substantiated by the experimental observations.

4. The development of field-assisting potential and its relation with vacancy concentration have been indicated through consideration of the incorporation equilibrium step at the oxide/oxygen interface.

5. The limiting thickness values for different conditions of experimentation on copper and its alloys studied so for have been found to be explainabe in a quantitative way through the assumption of prohibitive activation energy idea.

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REFERENCES

1. N. F. Mott and R. W. Gurney, *"Electronic Process in Ionic Crystals,"* Dover Publication (1964).
2. F.W. Young, J.V. Cathcart and A.T. Gwathmey, *Acta Met.*, 4 (1956) 145.
3. N. F. Mott, *Trans Faraday Soc.*, 43 (1947) 429.
4. N. F. Mott, *J. Chem. Phys.*, 44 (1947) 147.
5. N. F. Mott and N. Cabrera, *Reports Prog. in Phy.*, 12 (1948–49) 163.
6. N. Cabrera, *Phil. Mag.*, 40 (1949) 175.
7. K. Hauffe, "Oxidation of Metals," Plenum Press, New York (1965).
8. H. H. Uhlig, *Acta Met.*, 4 (1956) 541.
9. J. N. Butler, *J. Chem. Phy.*, 35 (1961) 636.
10. A. T. Fromhold, *J. Phy. Chem.*, Solids, 24 (1963) 1309.
11. J. E. Boggio and R. C. Plumb, *J. Chem. Phy.*, 44 (1966) 1081.
12. K. Hauffe and B. Illschner, *Electrochem.*, 58 (1954) 467.
13. A. T. Fromhold and E. L. Cook, *J. Chem. Phy.*, 44 (1966) 4564.
14. N. F. Mott and E. P. Fehlner "Oxidation of Metals and Alloys," A.S.M., Ohio, p-37 (1970).
15. T. N. Rhodin, *J. Amer. Chem. Soc.*, 72 (1950) 5102.
16. T. N. Rhodin, *J. Amer. Chem. Soc.*, 73 (1951) 3143.
17. B. Lustman and R. F. Mehl, *Trans. Amer. Ins. Min. Met., Eng.*, 143 (1941) 246.
18. J. A. Allen, *Trans. Faraday. Soc.*, 48 (1952) 273.
19. H. A. Milley and U. R. Evans, Nature, 139 (1937) 283.
20. P.K. Krishnamoorthy and S.C Sircar, *J. Electrochem. Soc.*, 116 (1969) 734.
21. P.K. Krishnamoorthy and S.C. Sircar, *Acta Met.*, 16 (1968) 1461.
22. P.K. Krishnamoorthy and S.C. Sircar, *Corrosion*, 24 (1968) 407.
23. P. K. Krishnamoorthy and S. C. Sircar, *Scripta Met.*, 2 (1968) 255.
24. P.K. Krishnamoorthy and S.C. Sircar, Oxidation of Metals, 2(4) (1970) 349.
25. S.K. Koy, Ph.D., Thesis on "Kinetics of oxidation of copper and its alloys at low and intermediate temperatures," Indian Institute of Technology, Kharagpur, India (1976).
26. C. Wagner and K. Grunewald, *Z. Phy. Chem.*, B40 (1938) 455.
27. T.B. Grimley, and B.M.W. Trapnell, *Proc. Roy. Soc.*, A234 (1956) 405.