EFFECT OF VARIOUS VARIABLES ON THE KINETICS OF OXIDATION OF COPPER

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MASTER OF ENGINEERING
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(Extractive Metallurgy)

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CERTIFICATE

CERTIFIED that the dissertation entitled 'Effect of various variables on the kinetics of oxidation of Copper', which is being submitted by Mr. Rajesh Chandra Arora in partial fulfilment for the award of Degree of Master of Engineering in Metallurgical Engineering (Extractive Metallurgy) of University of Roorkee, Roorkee is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this dissertation has not been submitted for award of any other degree or diploma.

This is further to certify that he has worked for a period of nine months from January, 1971 to September, 1971 for preparing this dissertation at this University.

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PREFACE

Annually, large amounts of copper and its alloys are being lost due to scaling at high temperature in the oxidising atmosphere. This attracted the attention of many workers to study the oxidation kinetics under various conditions. Studies of reaction rates and kinetics provide valuable information about the reaction mechanism and the rate - limiting step of the total reaction. The scaling resistance of pure copper was found to improve by the addition of various alloying elements such as Aluminium, Silicon, Tin etc. The majority of the published work refers to the oxidation of pure copper yet some work has been reported on the influence of various other metals on its oxidation kinetics.

In the present investigation an attempt has been made to study the oxidation of pure copper in air in the temperature range 500-900 °C. Further the effect of various additives , such as Aluminium, Zinc, Tin, Silicon, Cadmium and Manganese on the oxidation kinetics of pure copper has also been studied.

The dissertation has been presented in three chapters. The first chapter deals with the review of literature on the mechanism and kinetics of oxidation of Copper and its alloys. It also includes a brief account of the work reported so far on the effect of Alloying on Oxidation of pure Copper.

The second chapter includes the description of the experimental set-up and procedure followed in this investigation. The results obtained from the experiments conducted and a discussion on them constitutes the subject matter of the third chapter.

Analysis of the results shows that the Oxidation of Copper above 600°C, follows a parabolic law. While at 500°C, the initial stage of Oxidation depart significantly from the parabolic law and the Oxidation seems to follow a logarithmic law.

Out of the alloys investigated the most oxidation resistant were those containing aluminium (7%) or large amount of Zinc (20-40%) at all temperatures from 500 to 900°C. The next were those containing Silicon (7%) at all temperatures from 500 to 700°C. Addition of 7% Tin also imparts good oxidation resistance. Manganese (7%) and Cadmium (7%) have very little effect in the same temperature range. Attempt has been made to correlate the effect of alloying elements on the basis of electrical conductivity of the oxides of the additives as proposed by Wagner. It has been seen that the alloying elements having low electrical conductivity e.g. Al, Si, impart higher resistance to oxidation except for Zinc and Tin which gave higher resistance in - spite of having higher electrical conductivity. This may be attributed to the fact that the oxides of these metals are Excess - Cation type semiconductors.

ACKNOWLEDGEMENTS

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RcArora

(R.C. ARORA)

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CHAPTER-I

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I

MECHANISM AND KINETICS OF OXIDATION OF COPPER AND ITS ALLOYS

I.1. INTRODUCTION

During the past three decades considerable work has been carried out in the field of high-temperature oxidation of metals and alloys[1-3]. Forty years ago, oxidation problems were tried to be solved in a purely empirical manner, as neither thermodynamic nor kinetic data were available. As the data were determined gradually, attention was then drawn to true reaction mechanism. In the recent years an increased emphasis has been given to establish the fundamental aspects of metal - Oxygen reactions and an improved understanding of the oxidation behaviour of metals. This development, to a large extent has been due to an increased availability of improved equipment and the use of more refined experimental techniques.

The oxidation behaviour of Copper under a wide variety of conditions has been studied extensively.[4-7] Of the early workers in this field, mention may be made of Pilling and Bedworth[4] (1923), Dunn[8] and Tylecote[9]. Wagner[10] developed a theory of Parabolic oxidation which has proved to be very useful and may well lead to a more complete understanding of the mechanism of oxidation of alloys.

This theory has been found to be well applicable in case of oxidation of pure Copper, where the reaction obey the parabolic time law.

I-2. MECHANISM OF OXIDATION

When a clean metallic surface is exposed to air or oxygen, the initial step in the metal-oxygen reaction involves the adsorption of gas on the metal surface. As the reaction proceeds , the oxide is formed on the surface either as a film or as a seperate oxide nuclei. Both the adsorption and the initial oxide formation are functions of surface orientation, crystal defects at the surface, surface preparation and impurities in both the metal and the gas.

The surface oxide, in turn, separates the metal and the gas. When a compact film covers the surface, the reaction may proceed only through a solid -state diffusion of the reactants through the film. It is unlikely that Oxygen will pass inwards, except through cracks, but since the radius of the cations of the metal under consideration is much smaller than that of the oxygen ion, prospects of metal diffusing outwards are more favourable. Although cuprous oxide is generally writen as Cu_2O, analysis shows that it generally contains slightly less metal than required by the formula. It is believed that in general cuprous oxide has a certain number of vacant places on its cation lattice, and that an equivalent number of cations are cupric instead of cuprous, thus preserving electrical conductivity, so it is clear that such an oxide film, movement of metal ion is possible , even in the absence of continuous pores. A copper cation next to a vacant place can move into that place, leaving behind a new vacant place into which another cation can follow. Thus if a plate of copper covered with a cuprous oxide film is exposed to air, the Cu can move outwards through the film. So a mechanism for continued oxidation has been provided, but the passage will become increasingly slow as the film thickens and the rate of oxidation falls.

The movement of the Copper cations must be accompanied by an outward movement of electrons,otherwise an electric charge would accumulate. When the electrons arrive at the outer surface of the film, they react with the oxygen atoms already adsorbed, converting them to $O^=$ ions, which take their places in oxide lattice. Fresh oxygen atoms are then adsorbed. Thus the oxide film steadily grows outwards.

Pilling and Bedworth[4] have shown that when the diffusion through cuprous oxide film becomes sufficiently difficult, cupric oxide is developed in the films presumably from the oxidation of cuprous oxide. This is due to the fact that when the Cu_2O film is thin, the outward diffusion of Copper is so rapid that it can take up the available oxygen at the outer surface of the film and forms Cu_2O, but as the film thickens, the outward diffusion of copper decreases and oxygen becomes available for conversion of cuprous to cupric oxide.

In addition to the growth of oxide nuclei and crystallites, oxide crystals have also been observed to grow in the shape of whiskers. Ronnquist[6] studied the oxidation of copper at 170-500°C. He observed that the above 325°C, the oxide whiskers were randomly distributed over the surface amd the growth of whiskers never occurs during the initial stage of oxidation but is always associated with oxide films or scales. Oxide crystals are single crystals. The whiskers formed are of CuO. Whiskers may grow by several mechanisms. Pfefferkorn[11] has shown that CuO whiskers grow at the tip and the growth was reported to be linear with time. The amount of oxide contained in the whiskers represents a minor part of the total surface oxide.

I-3. NATURE OF OXIDATION PRODUCT

Pilling and Bedworth[4], Tylecote[9] and Ronnquist[7] have found that the thin films formed on copper consist of cuprous oxide but when the film becomes thicker, a sooty deposit of black cupric oxide appears outside the cuprous film. The relative thickness of the CuO layer tends to decrease as the oxidation temperature increases, since CuO dissociates at 1025 °C. At 500 °C, the scale consists of a very thin layer of Cu_2O adjacent to the metal followed by a thick layer of CuO, whereas the scale at 900 °C was found to consist mainly of Cu_2O with an outer skin of black CuO. It has been shown[12] that this type of CuO layer does not appreciably affect the normal kinetics of oxidation of copper and its alloys.

Valensi[13] has shown by theoretical treatment that ideally the composition of the oxide film on copper should vary with temperature from 98% CuO at 300°C to 90% Cu_2O at 900°C, and has given experimental figures which agree well with the calculated ones as shown in Table 1.

TABLE-1 % OF CuO IN THE OXIDE LAYER (Valensi[13])

TEMPERATURE	% CuO CALCULATED	% CuO EXPERIMENTAL
900	10.0	5.0
700	20.0	30.0
500	75.0	80.0
300	98.0	95.0

Fig.1 shows the comparision between the calculated and experimental composition of product of oxidation of copper.

Tylecote[9] has concluded that the composition of oxide film on copper is related to its total thickness. The

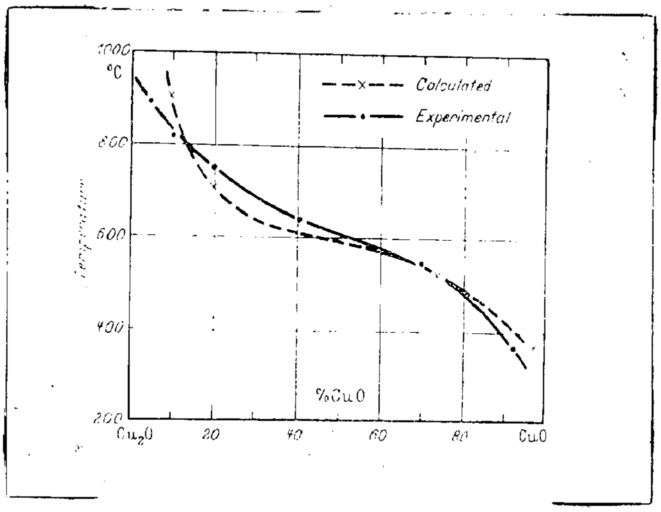

Fig.1 Composition of the Oxide Film formed on Copper(Valensi[13]).

thickness is a function of temperature at which the film is produced, the period or time during which it is formed, the oxygen concentration in which it is developed and any factor that might alter the permeability of the film e.g. state of original surface, thermal stressing due to temperature cycle etc.

EXFOLIATION OF SCALE

In case of pure copper and most of its alloys the exfoliation of scale takes place during cooling after oxidation. Tylecote[9] and others[5,6,7] have attributed it to the fact that the contraction of the metal in general will be greater than that of the oxide which imposes a compressive stress on the oxide and this leads to exfoliation on cooling. This could be easily visualised on seeing following data:

Thermal coefficient of Cu - $0.73 \times 10^{-6}/^{\circ}C$

Thermal coefficient of Cu_2O - $17 \times 10^{-6}/^{\circ}C$

I-3. RATE EQUATIONS GOVERNING OXIDATION

Pilling and Bedworth[4] have found that the oxidation of pure copper takes place according to the parabolic relation - the square of the weight increase being proportional to the time of oxidation:

$$w^2 = Kt$$

Where w is the weight increase per unit area.

t is the time

k is a constant

Tylecote[9] has observed that above 700°C, the oxidation of copper is governed by parabolic law and the results were found to be in good agreement to those of Pilling and Bedworth[4]. But at lower temperatures there were departures from this relationship and the logarithmic law have been found to be valid.

$$w = W \log_e \left(\frac{t}{t_o} + 1 \right)$$

Where W and t_o are constants, having the dimensions of weight per unit area and of time respectively, t is the time, and w is the weight increase per unit area.

The mode of transition of mechanism of oxidation from the low temperature to the high temperature is of interest. It has been proposed that at any particular temperature the low temperature mechanism persists only to a certain film thickness, after which the parabolic mechanism becomes operative.

Pilling and Bedworth[4] have established that if the rate controlling step is a transport of material across the layers, the rate of transport and hence the overall reaction rate decreases with time. This has been attributed to the fact that the layer becomes proportionately thicker through which the material has to be transported.

I-5. THEORIES OF OXIDATION

The most important single contribution to the understanding of high temperature oxidation of metals has been given by Wagner[10] thirty years ago, and is still the most versatile among the various theories of oxidation, since it applies to many metals and alloys. The only limitation of this theory is that it is not applicable in cases where thin film is formed. In such cases Mott's theory has been found to be valid.

WAGNER'S THEORY

According to Wagner's theory , the electrical conductivity of the oxide film influence the oxidation rate to a very great degree, and oxides with low conductivity should produce films with high oxidation resistance and vice-versa. The Cu_2O film formed during the oxidation of Copper is a metal-deficiet (p type) semiconductor. The cation lattice contains some vacant sites (Figure 2), and the electrical neutrality is established by the formation of cations of higher valency. The number of higher valency ion is identical with the number of 'electron defects' and the number of electron defects determine the electrical conductivity.

Wagner[10] has shown a schematic representation of diffusion in the system $Cu-Cu_2O-O_2$.(Figure 3). Quantitatively one oxygen molecule would effect the migration of four Copper ions (Cu^+) and four electrons with the formation of four vacant Cu^+ sites($\square Cu^+$) and four vacant

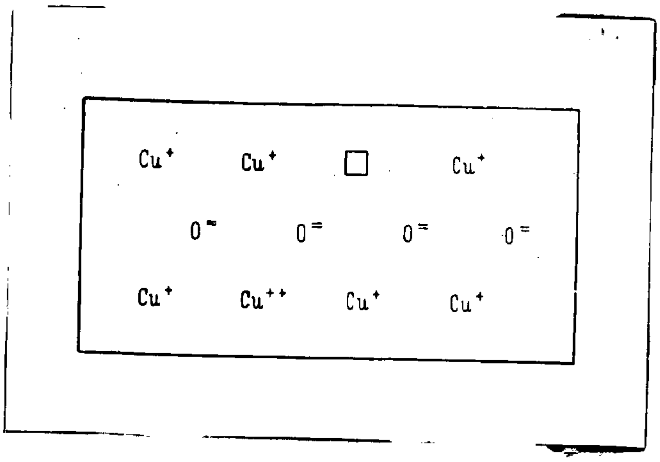

Fig.2 Structure of the Cu_2O Lattice.

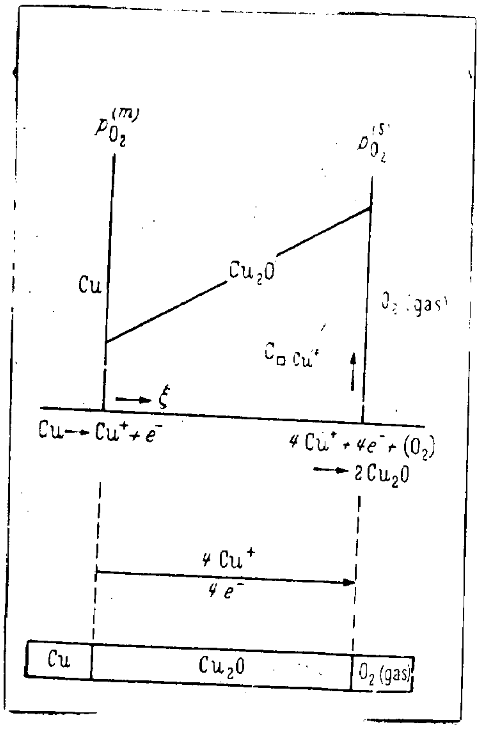

Fig.3 Schematic representation of diffusion in the System Cu-Cu_2O-O_2 (Wagner[10]).

electron sites ($\oplus$) :

$$O_2 = 4\,\square Cu^{+} + 4\oplus + 2\,Cu_2\,O \quad \text{-----------(1)}$$

If other disorder equilibria are negligible the concentration of the ion will be equal to concentration of electron defects.

$$\text{i.e. } c(\square Cu^{+}) = c\,(\oplus) \quad \text{-----------(2)}$$

It has been assumed that thermodynamic equilibrium is established between the oxide and oxygen gas at the oxide/oxygen interface and between the metal and oxide at the Metal/oxide interface.

The driving force of the reaction is the free energy change associated with the formation of the oxide $Cu_2\,O$ from the metal Cu and the oxygen gas, and as a result concentration gradients of the components are established in the oxide. (fig.3).

The partial pressure of oxygen at the metal/oxide interface is equal to the equilibrium dissociation pressure of the oxide in contact with its metal, $PO_2^{(m)}$, while at the oxide/oxygen interface it is equal to the oxygen pressure in the gas phase, $p_{O_2}^{(s)}$. As $p_{O_2}^{(s)} > p_{O_2}^{(m)}$, the metal ion vacancies are continously produced at the MO/O_2 interface and consumed at M/MO interface.

Wagner[10] has derived an expression for the rate of thickening in terms of the specific conductivity of the film (λ in Ω^{-1} cm^{-1}), the transport numbers of the cations, anions and electrons (t_c, t_a, t_e), and the free energy decrease of the oxidation reaction (E_0 in volts). The most simple form of Wagner's equation is given below:

$$\frac{d\eta}{dt} = \frac{(t_c + t_a)\ e\ \lambda\ A\ E_0}{96500}$$

Hoar and Price[16] have derived similar equation on the basis of electrochemical model, which gives a very clear picture of the fundamental processes involved. In this, the transport of both ions and electrons through an oxidation layer have been considered as a flow of current through a cell in which the oxide scale simultaneously serves as an electro-lyte for the ionic transport and as a circuit for transport of electrons. The electromotive force of the cell is the decrease in free energy of the reaction, Eo. Fig.4 shows the electrochemical model of the oxidation of a metal Me by a gas X_2.

The cathodic reaction at the film - gas interface is represented by

$$X + e^{-} = X^{=} \quad \text{or } O_2 + 4e^{-} = 2O^{--} \quad \text{--------(3)}$$

The anodic reaction takes place at the metal-film interface and corresponds to $Me = Me^{+} + e^{-}$ --------(4)

The total resistance of the cell is the sum of the

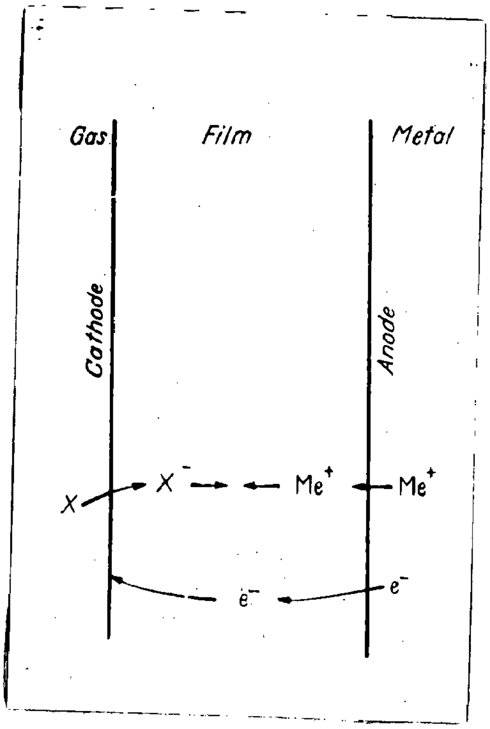

Fig.4 Electrochemical Model of Oxidation(Hoar & Price[16]).

the electrolytic plus electronic resistances. If the cell has an area A (cm^2) and film thickness ξ (cm), then the total resistance equals

$$R_{total} = \left\{ R_{electrolytic} + R_{electronic} \right\} \frac{\xi}{A}$$

$$= \frac{\xi}{A(t_A + t_c)} + \frac{\xi}{A\, t_e\, \chi}$$

$$= \frac{\xi}{(t_a + t_c)\,.\, t_e\,.\chi\cdot A} \qquad \text{---------(5)}$$

since $t_A + t_c + t_e = 1$

If the area of the film consists of n g - equivalents and is formed in t second and if the rate of film growth is assumed to be equivalent to the current I (Amp), Faradays and Ohms' law yield

$$\frac{dn}{dt} = \frac{I}{F} = \frac{Eo}{FR} \qquad \text{-------(6)}$$

Hence $$\frac{dn}{dt} = \frac{(t_c + t_a)\; t_e\; \chi\, A}{96500\, \xi} \qquad \text{--------(7)}$$

This is the most simple form of the equation derived by Wagner[10].

$\frac{dn}{dt}$ is proportional to the rate constant k_p in the parabolic law of film growth, actually

$$\frac{dn}{dt} = \frac{1}{2}\, V_{eq}\, (Z/M)^2\, k_p \qquad \text{-------(8)}$$

Where V_{eq} = volume of 1g -equivalent of the oxide.

Z = valency of oxygen ion

M = atomic weight of oxygen.

Equation (7) has been used as a first approximation to calculate rate constants. Dunwald and Wagner[17] obtained the transport number of cations and anions for cuprous oxide:

$$\tau_{cu} + \tau_{O^{--}} = 4 \times 10^{-4} \quad (\tau_e \text{ therefore} \approx 1)$$

and $\kappa = 4.8\ \Omega^{-1}\ Cm^{-1}$ at 1000^{o} c and an oxygen pressure of 8 mm Hg.

The emf of the reaction $2\ Cu2^{O} = 4\ Cu + O_2$ has been calculated from the free energy equation to be equal to 0.337 V at 1000^{o} C and p_{O_2} =100 mm Hg.

With these data and taking unit area and thickness of the film, the reaction rate was obtained by means of equation

$$\text{Reaction rate } \frac{dn}{dt} = 6.7 \times 10^{-9} \text{ g - equivalents x } cm^{-1}\ sec^{-1}$$

According to Feitknecht's[18] results, which were found to be in good agreement with others , the rate constant k_p equals $8 \times 10^{-8}\ g^{2}\ cm^{-4}\ Sec^{-1}$ (for $\theta = 1000^{o}$ C and p_{O_2} = 100 mm)

From this

$$\frac{dn}{dt} = \tfrac{1}{2}\,Veq\left(\frac{Z}{M}\right)^{2} k_{p} = \tfrac{1}{2}\ \frac{23.3}{2}\left(\frac{2}{16}\right)^{2} 8\times 10^{-8}$$

$$= 7 \times 10^{-9} \text{ g -equivalents } Cm^{-1}\ sec^{-1}$$

which is in very good agreement with the value of 6.7×10^{9} calculated above despite the simplifications involved in deriving equation (7).

I.5.2 THIN FILM THEORY

This theory is based on the hypothesis that a strong electric field is set up in the thin oxide film. In the mechanism suggested by Cabrera and Mott[19,20], it has been assumed that a Chemisorbed film exists on a metal and that ions and electrons move independently in the film. At low temperatures the ions cannot simply diffuse through the film due to a concentration gradient of ions but the electrons were supposed to pass from the metal to the oxygen adsorbed on the surface of the film, either by thermionic emmission or, more probably by the so called tunnel effect. Tunnel effect is a quantum - mechanical process by which electrons of lower maximum energy than that of a barrier possess a finite probability of penetrating this barrier.

In this case cations would be formed at the metal oxide interface, and oxygen anions at the oxide- gas interface. Thus a strong electric field would exist across the oxide film which would be mainly responsible for pulling the ions through the film. The transfer of the metal into the oxide at the metal/oxide interface was assumed to be rate - determining. It has also been assumed in this model that the defect concentrations are constant within the film. This model has a limitation that it is only valid for oxide thickness smaller than 20Å, which is the largest thickness from which sufficient electrons can tunnel through the oxide.

The oxide film growth has been represented by an equation.

$$\frac{1}{x} = A - K_{il} \log t \qquad \text{--------- (9)}$$

which is the inverse or reciprocal logarithmic rate law.

In the earlier work Mott[21] has also proposed a model in which electron tunneling through the oxide film is rate - determining and on this basis, he has derived a direct logarithmic rate equation for the growth of oxide films which can be expressed by

$$x = k_{log} \log t + k_2 \qquad \text{--------(10)}$$

In other treatments of low-temperature oxidation of metals the effects of space charge in the oxide films has also been taken into consideration. Uhlig[22] has derived a logarithmic rate equation assuming that the oxidation rate is controlled by electron flow from the metal to the oxide. It suggests that the electron flow is a function of space charges set up near the metal/oxide interface. The space charge is found to change with time, as increasing numbers of electrons become trapped at lattice defect sites.

I.6. OXIDATION OF ALLOYS

The mechanism and kinetics of oxidation of pure copper can be altered significantly by the additions of alloying elements. The mechanism of oxidation is much complex incase of copper alloys than in pure copper. This is due to the fact that the components of alloys have different affinities for oxygen and the reacting atom do not diffuse at the same rates either in the oxide or the alloy phases. As a result, oxide scales on alloys will not contain the same relative amounts of the alloy constituents as does the alloy phase. Further-more the composition and structure of the oxide scales on alloys will often change as the oxidation proceeds, and the oxidation kinetics, in turn, often markedly deviates from the ideal and simple rate equations .

Other complicating factors arise if oxygen dissolves in the alloy phase, the least noble alloy component also forms oxide inside the alloy (Internal Oxidation). Owing to this complexity it is often difficult to give an overall quantitative description of oxidation of alloys. In copper alloys selective oxidation and subscale formation has been reported.

SELECTIVE OXIDATION

Selective oxidation has been found[4] to occur in alloys for which the oxides of alloying elements show large difference in stability e.g. Aluminium, Silicon or Beryllium etc. In this the least noble constituent of an alloy is selectively oxidized to form an outer, protective layer. However the occurance of selective oxidation is dependent not only on the type of alloying addition but also on the concentration of the active alloying component, on temperature and on partial pressure of oxygen. Under any set of conditions selective oxidation will take place only above a critical concentration of the active alloy compoent.

Wagner[14,15] has analysed the condition necessary for selective oxidation in a binary alloy and has derived a mathematical expression for this critical concentration.

Wagner[14,15] has considered an alloy A-B in which A and B do not react to form a double oxide and B is the less noble metal. Assuming that compact scales are formed, three cases of oxidation may be considered.

<u>Ist Case.</u> At low concentrations of B, only the oxide of A will be formed and B will diffuse into the alloy from the alloy/oxide interface. As the oxidation proceeds further, the concentration of B in the alloy will increase and the formation of B oxide will take place when the concentration of B at the interface reaches the equilibrium concentration of B, N_B^*, in the mixture (alloy

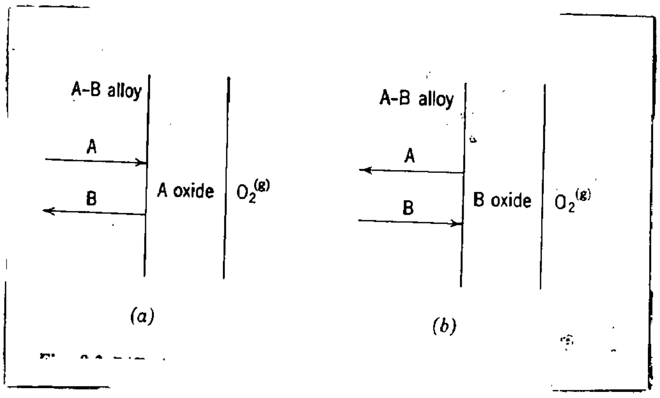

Fig.5 Diffusion Processes during Oxidation of Alloys.

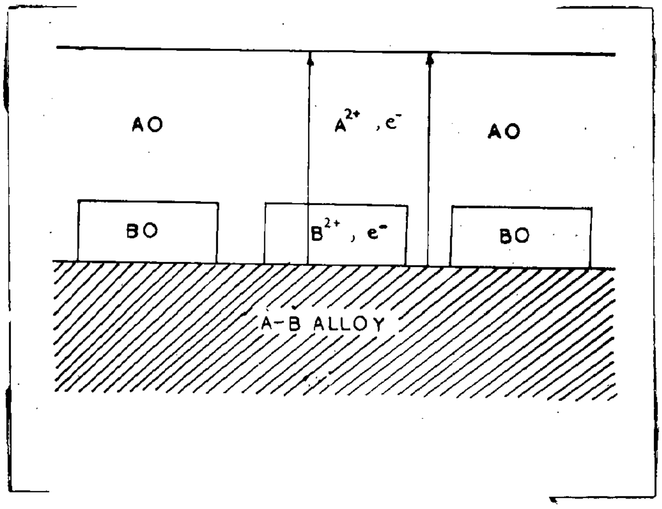

Fig.6 Composite Scale Formation in Alloys.

+ A oxide + B oxide). (Fig.5 a). The concentration of B in the bulk alloy, N'_B, is smaller than N^*_B.

2nd Case: If the concentration of B in the alloy is sufficiently high, N''_B, then only the B oxide will be formed and A will diffuse into the alloy from the alloy/oxide interface (Fig.5 b). The formation of the A oxide will begin to take place only when the concentration of A at the interface reaches the critical composition.

$$N^*_A = 1 - N^*_B \qquad \text{---------------}(11)$$

corresponding to the three phase equilibrium (alloy + A oxide + B oxide). It follows from this mechanism that $N''_B > N^*_B$.

3rd Case:

Between the above two ranges (from N'_B to N''_B) is the third range in which the A oxide and the B oxide will simultaneously be formed. (Composite scales). A possible reaction mechanism for this case, assuming that cations are mobile species and AO grows more rapidly than BO, is shown in figure 6 . B oxide grows according to the displacement reaction:

$$AO + B^{2+} = A^{2+} + BO \qquad \text{--------------}(12)$$

Assuming the formation of a compact,pore-free oxide scale, Wagner[14] showed that the critical concentration N_B'', above which the B oxide is formed is given by:

$$N_B'' = \frac{V}{Z_B M_o} \left(\frac{\pi k_p}{D} \right)^{\frac{1}{2}} \quad \text{------(13)}$$

Where V is the molar volume of the alloy.

Z_B is the valency of the B atoms.

M_o is the atomic weight of Oxygen.

D is the diffusion coefficient of the B in alloy.

k_p is the parabolic rate constant for exclusive formation of the B oxide ($k_p = (m/A)^2/t$)

In case of Copper-Beryllium alloys, the critical concentration for the exclusive formation of BeO has been theoretically calculated from the above relationship, taking V to be equal to 7.1 cm^3/g-atom, $Z_{Be} = 2$, $D = 10^{-9}$ cm^2/sec. and $k_p = 2 \times 10^{-12}$ g^2/cm^2 sec. From these data the critical concentration of Beryllium for the exclusive formation of BeO comes out to be equal to 1.8 at%.

Similarily the critical concentration for the selective oxidation of other alloying elements can be calculated by knowing the value of diffusion coefficient, valency, molar volume of the alloy and parabolic rate constants.

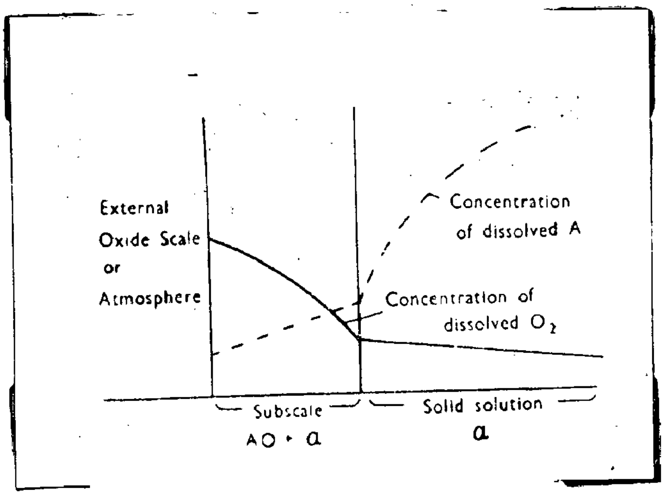

Fig.7 Concentration of Oxygen and Solute in Solid-Solution.

INTERNAL OXIDATION AND SUBSCALE FORMATION

Copper base alloys in which oxygen is relatively soluble may develop a subscale or zone of internal oxidation. Underneath the scale proper is a layer consisting of Copper with oxygen in solution and containing small particles of the oxide of the alloying element. This layer was termed 'subscale' by Smith[24], and the effect is known as 'internal oxidation. This effect is due to the diffusion of oxygen into the alloy, resulting in the preferential oxidation of the alloying element and its precipitation as insoluble oxide. Figure 7 shows the concentration of oxygen and solute in solid-solution.

Smith[24] has noticed that in case of Copper-Silicon alloys, a subscale consisting of a precipitate of silica embedded in a matrix of metallic copper containing some oxygen in solid-solution is formed. He stated that an essential requirement for the formation of subscale is that an appreciable, although possibly very small, solubility of oxygen in Copper.

Frohlich[27] has shown that all alloys containing metals more negative than Copper exhibit internal oxidation to dome degree.

I-7. EFFECT OF VARIOUS ALLOYING ELEMENTS ON THE OXIDATION KINETICS OF COPPER

Comprehensive reviews have been published on the oxidation kinetics of Copper base alloys by Tylecote[9], Preece and Dennison[5] and Dunn[8]. Out of the alloys investigated the most oxidation-resistant were found to be those containing Aluminium, Beryllium or Magnesium. The next to them were alloys containing large amounts of Tin or Zinc. The effect of additions of Chromium or Arsenic were found to increase the oxidation rate.

Kubaschewski and Hopkins[1] have summarised the work so far reported on the effect of alloying elements on the oxidation kinetics of pure Copper into a simple graph (figure 8 and 9). The ordinates in the diagram indicates (F), the alloying factor of oxidation and concentration of the alloying elements. F is the ratio of the oxidation rate (Δm) of the alloy to that of pure copper,i.e.

$$F = \frac{\Delta m \text{ alloy}}{\Delta m \text{ Copper}} \qquad \text{-------------}(14)$$

This plot serves as a qualitative indications of what sort of result can be expected with a particular binary alloy,or which elements may profitably be added to Copper to improve the oxidation-resistance. The effect of various additives are as follows:

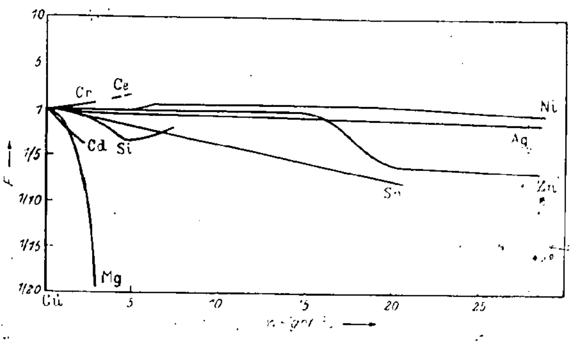

Fig.8

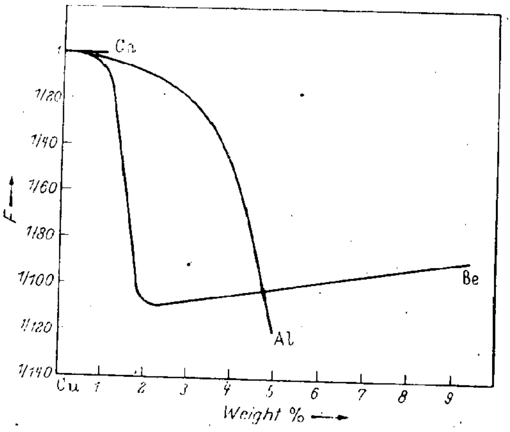

Fig.9

Fig.8&9 Experimental data compiled by Kubaschewski & Hopkins[1] on the effect of alloying on oxidation. of Copper.

EFFECT OF ZINC

Dunn[24] observed the oxidation of Copper-Zinc alloys containing from 60 to 100% copper in air at temperatures from 580 to 880°C. In alloys containing from 28 to 40% zinc the scale was found to consist of ZnO, while in the alloys containing 0-12% Zinc the scale contained copper in the same proportion as in the alloy. In these two groups the rate of oxidation at constant temperature was found to obey the parabolic law, but for the intermediate range of alloys (12-28% Zn) the oxidation rate was found to be much less than that corresponding to the parabolic law and the departure has been attributed to an increase in the grain size of the film.

Rhines and Nelson[26] have also shown that, in oxidation of Cu-Zn alloys at 800°C, alloys with less than 10 at % Zinc obey parabolic rate which is approximately equal to that of pure copper. (Figure 10). Between 10 and 20% Zn the oxidation rate decreases with increasing Zinc concentration, while above 20% the reaction rate becomes independent of alloy composition.

For alloys containing between 10 and 20 at % Zn the composition of the scale changes sharply with alloy composition. Further more it has been found that such alloys do not follow a parabolic reaction behaviour. (figure 11). Levin and Wagner[12] predicted such a behaviour due to changes in the composition of the scale with time and to the following displacement reaction:

$$\mathrm{Zn\ (in\ alloy)} + Cu_2O = 2\,Cu + ZnO \quad \text{--------}(15)$$

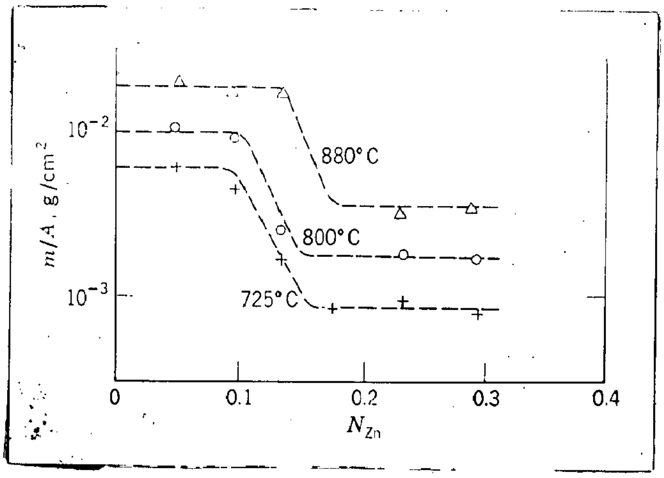

Fig.10 Weight increase9(g/cm^2) of Cu-Zn alloys after 5 hr. of oxidation in 1 atm O_2(Dunn[8])

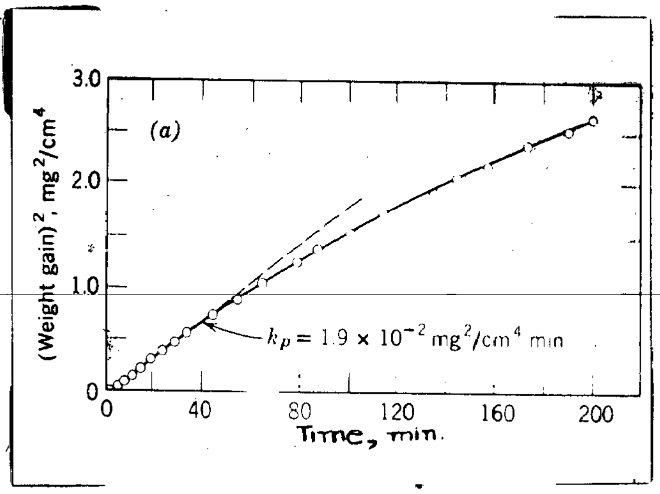

Fig. 11 Parabolic plot of oxidation of Cu-15%Zn alloy in 1 atm O_2 at 700°C(Levin & Wagner[12]).

occuring in the scale during oxidation.[24,12] The free energy of formation of the respective oxides of Zinc and Copper at 700°C is as follows:

$$\Delta G^{o}_{ZnO} = 60.5 \text{ k Cal/mole}$$

$$\Delta G^{o}_{Cu_2O} = 23.7 \text{ k Cal/mole}$$

and the above equation thus proceeds to the right.

Wagner[14] has also predicted that with mole fraction of $N_{Zn} \simeq 0.15$ there would be exclusive formation of Zinc oxide.

EFFECT OF ALUMINIUM

The effect of aluminium on the oxidation kinetics of Copper has been studied by Frohlich[27], Price and Thomas[25] and Dennison and Preece[5]. The resulting Al_2O_3 scale provides excellent oxidation resistance. Frohlich[27] found that 5 at % Aluminium is needed to achieve the formation of a protective Al_2O_3 layer when oxidized inair at temperatures above 800°C, however, the same aluminium content does not result in selective oxidation; rather islands of Al_2O_3 are formed in the Cu_2O layer. The reason for this dependence on temperature has been attributed to the difference in activation energy of the diffusion of Al in Cu-Al alloys and that of copper. The former has a higher activation energy and so only at higher temperatures, the rate of diffusion of Aluminium in the alloy is sufficiently rapid to lead to exclusive formation of Al_2O_3.

Price and Thomas[25] found that at reduced partial pressure of oxygen, selective oxidation of Aluminium may be achieved in alloys with less than 5 at%.

Dennison and Preece[5] studied the oxidation of Copper-Aluminium alloys at temperatures between 400- 1000°C (Figure 12). They found that a double inflection occurs for the 2 and 4% Al in the temperature range 700°- 800°C. The minima in the rate curve at about 850°C was found to correspond to a more adherent type of scale i.e. to the presence of a more continuous and compact film of Al_2O_3 at the scale /metal interface. In the temperature range 400 to approximately 800°C, the scale was found to consists of Cu_2O containing alumina particles in the initial stages; and during further oxidation Cupric Oxide formation was indicated, and with prolonged periods of exposure the proportion of cuprous oxide was found to diminish until finally the scale consisted only of CuO and Al_2O_3. Above 875°C, Cupric oxide becomes unstable and so was not found in the scale. This scale was found to be non-adherent and consists of an outer layer of cuprous oxide containing alumina particles distributed along grain boundaries, which probably correspond to the grain boundaries of the original metal.

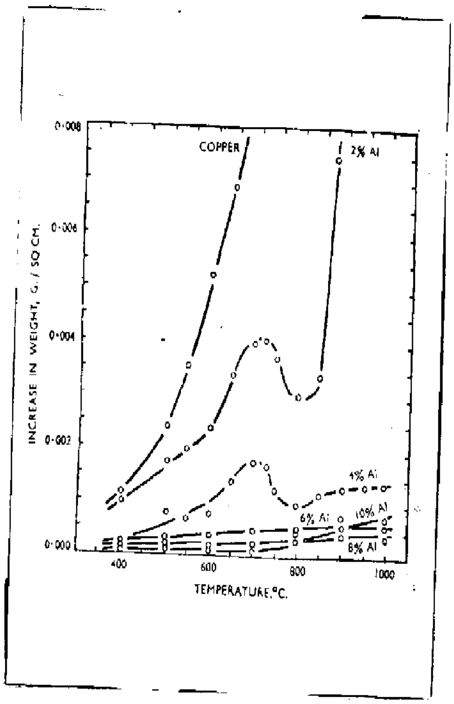

Fig.12 Oxidation of Cu-Al alloys after 24 hr at 400°C-900°C (Tylecote[9]).

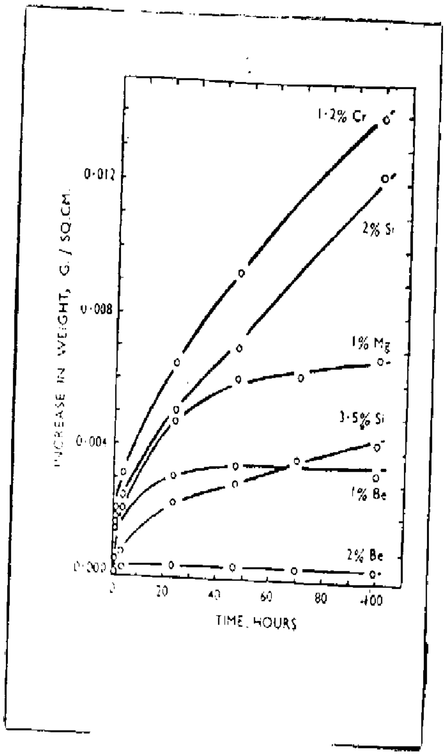

Fig.13

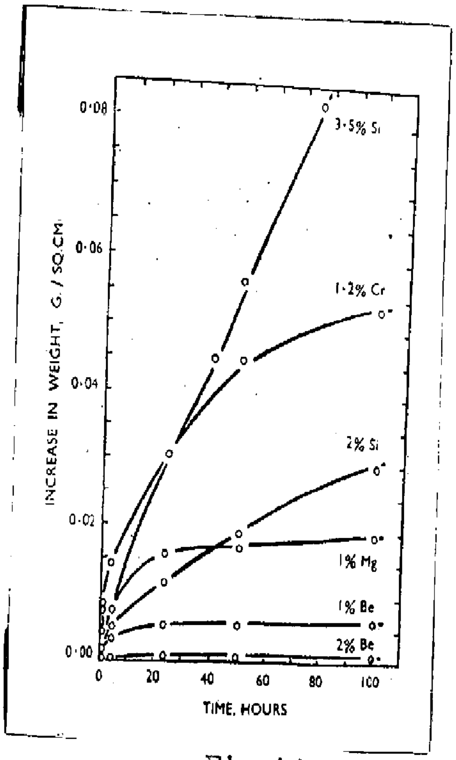

Fig.14

Fig.13 & 14 Oxidation of 1% Mg, 1.2% Cr, 1% Be, 2% Be, 2% Si and 3.5% Si alloys at various times at 650°C and 850°C respectively (Tylecote9).

EFFECT OF BERYLLIUM

The effect of Beryllium on the oxidation kinetics of Copper has been studied by Frohlich[27], Maak[23] and Dennison and Preece[5]. Frohlich[27] concluded that the effect of Beryllium appears to be consisting of preferential formation of a very thin highly protective film rich in Be O attached directly to the alloy surface.

Dennison and Preece[5] studied the oxidation behaviour of Copper -Beryllium alloys in air in the temperature range 500° to 900°C . The addition of 2% Beryllium was found to be sufficient to give a stable protective film of Beryllia over the entire temperature range. Further they concluded that the formation of a continuous protective film is enhanced at higher temperature. This has been attributed ~~due~~ to the increased rate of diffusion of the alloying element at higher temperatures. The curves on weight gain vs time plot become asymptotic in a shorter time at 850°C than they do at 650°C. (Figure 13,14).

Maak[23] studied the oxidation of Copper-Beryllium alloys at 800°C in air. Alloys with 0.8, 0.6,2.7 and 6.7% Be, respectively, were found to oxidize with approximately the same rate as pure copper contradictory to the above finding. The oxide scale was found to consist of thin outer CuO layer, a Cu_2O layer and an inner two phase layer of Cu_2O + Be O. In addition, internal oxidation resulting in the formation of

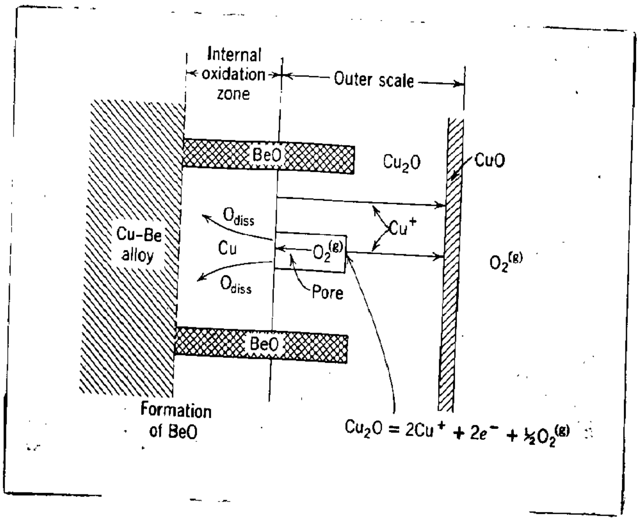

Fig.15 Schematic representation of Mechanism of Oxidation of Cu-Be alloys (Maak^{20}).

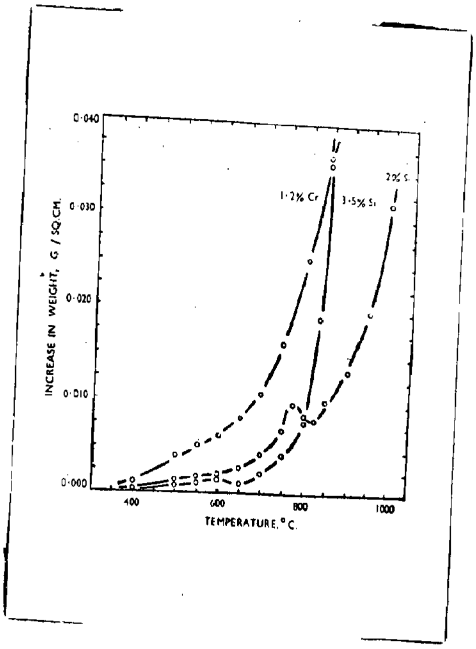

Fig.16 Oxidation of Copper-Silicon alloy and Copper-1.2% Cr alloy after 24 hr at 400°C-1000°C(Tylecote^9)

BeO crystallites in the Copper matrix occured beneath the scale /metal interface. A schematic diagram of the reaction mechanism of oxidation of Cu-Be alloys resulting in simultaneous formation of CuO, Cu_2O and BeO is shown in (Figure 15). 12.6 at % Be was found to be sufficient for the exclusive formation of BeO. In this case the oxidation was found to be 10^4 times slower than for Cu-Be alloys with less than 7 at% Be.

Wagner[14] has theoretically calculated the critical concentration for the exclusive formation of BeO to be equal to 1.8 at%. The discrepancy between the observed and the predicted value has been attributed ~~due~~ to additional factors which were not taken into consideration by the Wagner, e.g. internal oxidation of Be in the alloy, formation of porosity in the Cu_2O layer. Such porosity arises (when cations migrate by the vacancy mechanism through the scale) as a result of the accumulation of cation vacancies and interfacial detachment at the scale/metal interface.

EFFECT OF SILICON

Frohlich[27], Smith[24] and Dennison and Preece[5] have studied the effect of Silicon on oxidation kinetics of Copper. They concluded that there is a formation of subscale rich in copper but containing inclusions of the solute oxide. Evans and Chatterji[28] have studied the influence of 1 at% of Silicon on the high temperature oxidation of Copper in the temperature range 500 to 900°C. They have reported that the oxidation of the alloys follows a smooth parabolic law. The rates were found to be significantly slower than the corresponding values for pure Copper. The oxide scale was found to be similar to that on Copper but was less adherent and tended to flake off during cooling.

According to Dennison and Preece[5], the optimum Silicon content required for maximum resistance to oxidation was found to be 4%. The oxidation properties of Cu-2% Si were found to exhibit some interesting features. The rate curve shows a double inflection in the range 775-825°C (Figure 16). At temperatures 800°C and below, a film of Silica was observed at the scale/metal interface. Above 825°C the film of Silica was no longer evident and the inflections became more marked with increased time of exposure. Above 900°C there was evidence of partial melting at the surface of the metal.

EFFECT OF NICKEL

Pilling and Bedworth[4] concluded from their studies on effect of Nickel on Copper Oxidation that the oxidation resistance of Copper-Nickel alloys with upto 30% Ni is about the same as that of pure Copper. Above 30% Ni the oxidation resistance was found to increase a little. In the concentration range(30 to 80% Ni), the weight gain vs time curves were found to become linear and not parabolic. Hickman & Gulbransen[16], attributed the increase in oxidation resistance with increasing amount of Nickel, to the effect of Nickel on the diffusion - rate of Copper through the film.

EFFECT OF CHROMIUM

Dennison and Preece[5] found that the addition of 1.2% of Chromium to Copper confers no resistance to oxidation (figure 11). The structure of the oxide layer was found to be similar to that formed on Copper, except that the inner layer of cuprous oxide was found to contain particles of $Cr_2 O_3$.

The lack of protection has been attributed ~~due~~ to the low solid-solubility of Chromium, coupled with a low rate of diffusion in the Copper. The maximum solubility at the solidus is near 1.2% , but decreases rapidly at lower temperatures.

I-8. TEMPERATURE AND PRESSURE DEPENDENCE OF RATE CONSTANTS.

EFFECT OF TEMPERATURE

When oxidation is a simple diffusion process, i.e. when the parabolic law is obeyed, the temperature dependence of the oxidation rate should be in agreement with the Arrhenius equation:

$$K = A e^{-Q/RT} \qquad \text{-----------------(16)}$$

Where K is the rate constant $mg^2 Cm^{-4} hr^{-1}$

A is a constant ($mg^2 Cm^{-4} hr^{-1}$)

R is the gas constant

T is the absolute temperature

and Q the activation energy (cal.)

When the logarithm of the oxidation rate is plotted against the reciprocal of the absolute temperature, a straight line should result. The rate constants obtained by Pilling and Bedworth[4] and by Feitknecht[18] for Copper oxidized in oxygen, when plotted in this way, appear to fall on two straight lines intersecting at about 580°C (figure 17). The results of Hudson and his co-workers[29], and that of Vernon[30] - for Copper oxidized in air, when plotted in the same way, also gave two straight lines which were parallel to those of Pilling and Bedworth[4].

The scales formed on Copper between 300° and 900°C at normal pressure were found to consist of two layers, CuO overlying Cu_2O. The relative thickness of the CuO layer tends to decrease as the oxidation temperature increases, since CuO dissociates at 1025°C.

Valensi[13], has suggested that the upper part of the curve results from the reaction:

$$2\,Cu + \tfrac{1}{2}\,O_2 = Cu_2O \qquad \ldots\ldots\ldots\ldots(17)$$

For this reaction Valensi has obtained the formula by calculation and later confirmed the same by experiments. The rate constant was found to be :

$$K = 957\,e^{-37{,}700/RT} \qquad \ldots\ldots\ldots\ldots(18)$$

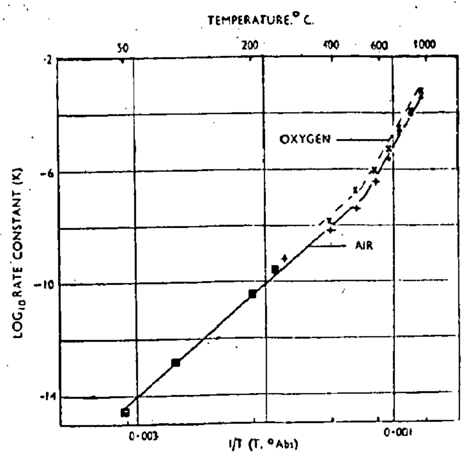

Fig. 17 Dependence of Oxidation Rate of Copper on Temperature(Tylecote[9]).

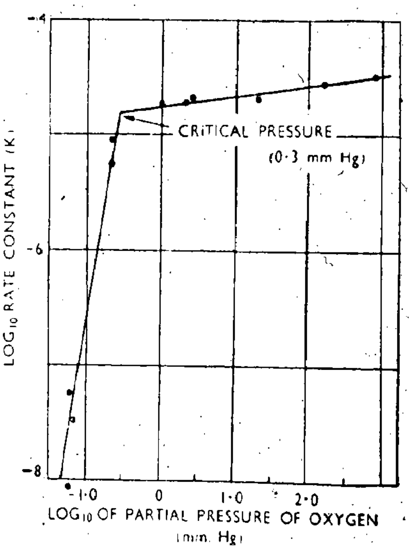

Fig. 18 Dependence of Oxidation Rate of Copper on Pressure (Pilling & Bedworth[4]).

At low temperatures, corresponding to those giving the lower straight line in the figure 17. Valensi[13] has given the rate determining reaction as:

$$Cu_2O + O_2 = 2\ CuO \qquad \text{.......(19)}$$

for which the value of K obtained by Valensi[13] is as follows:

$$K = 0.059\ e^{-20,140/RT} \qquad \text{........(20)}$$

Rate equations(18)&(20) define approximately the two straight lines shown in figure 17. These lines are according to Valensi, the extreme tangents of a curve, and at the intermediate temperatures the points in figures 17 represents a combination of reaction (17) and (19).

EFFECT OF GAS PRESSURE AND CONCENTRATION

By increasing the oxygen concentration, the proportion of CuO in the film has been found to increase by small amount[4] while by decreasing the oxygen concentration by the admission of nitrogen into the furnace atmosphere, the formation of CuO film can be prohibited entirely.

If the electrical theory of film formation is correct, increase in oxygen pressure should increase the electrical conductivity by increasing the number of ions and vacant spaces. Further Mott[31] has shown that if complete dissociation into ions and electrons takes place, the electrical conductivity should vary as $p^{1/8}$, but if no dissociation takes place as $p^{1/4}$.

Pilling and Bedworth[4] have shown that below 0.3 mm pressure the oxidation rate falls off far more rapidly (figure 18). They have proposed that at high pressures the diffusion of oxygen through the film is the controlling factor in the rate of oxidation and the film at the surface is fully saturated with O_2. As the pressure is reduced, a point is reached where the rate at which oxygen is absorbed becomes the controlling factor, the film surface ceases to be saturated with adsorbed oxygen, and a rapid decrease in oxidation rate results. At low pressures the rate of gas flow ~~past~~ over the heated specimen has been found to have a profound effect on the oxidation rate. This can be visualised from the table 2.

TABLE 2. EFFECT OF RATE OF GAS FLOW ON OXIDATION OF COPPER AT 800°C. (PILLING AND BEDWORTH)

RATE OF FLOW cc/mm	OXIDATION RATE CONSTANT (K) $g^2\ cm^{-4}\ hr^{-1} \times 10^{-7}$
In O_2 mixture; O_2 partial pressure: 1.7 mm Hg.	
14	0.046
95	0.77
110	10.0
245	36.0
550	70.0
In AIR; O_2 partial pressure: 155 mm Hg.	
Open furnace	270
15	250
145	260

I-9. METHODS OF STUDYING OXIDATION KINETICS

Various methods have been employed to study the oxidation kinetics of metals and alloys. One of the earliest and probably most commonly used, is the Gravimetric methods. Other methods are Volumetric, Manometric, Electrolytic and electron diffraction.

THERMOGRAVIMETRIC TECHNIQUE

By this technique, the increase in weight due to oxidation may be made with the help of a special balance. Kofstad and Anderson[32] have designed a quartz helix apparatus (figure 19) for thermogravimetric studies of the high temperature oxidation of metals. Reaction rates were followed by measuring the changes in the elongation of the helix with a Cathetometer. The sensitivity of a helix is a function of its length and diameter and the thickness of the wire or thread.

Gulbransen[33] has designed a vacuum microbalance which is more sensitive. A drawing of the apparatus has been reproduced in figure 20. In this method a specimen is suspended from the beam of a very sensitive, all quartz microbalance operating in all glass vacuum system. The tube is then sealed off. A scale micrometer microscope is used to observe the beam position relative to a fixed point on the supporting frame.

VOLUMETRIC & MANOMETRIC METHODS

The consumption of oxygen during oxidation may also

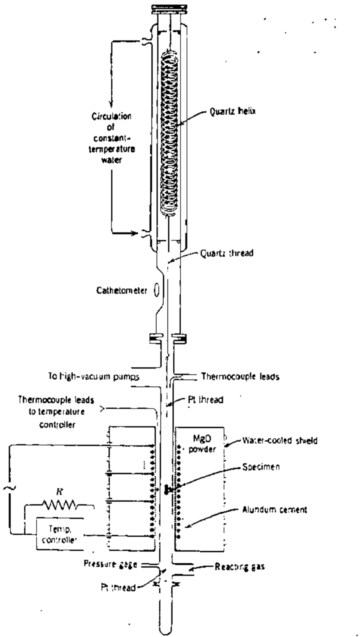

Fig. 19 Quartz helix apparatus for Thermogravimetric Studies (Kofstad & Anderson[32]).

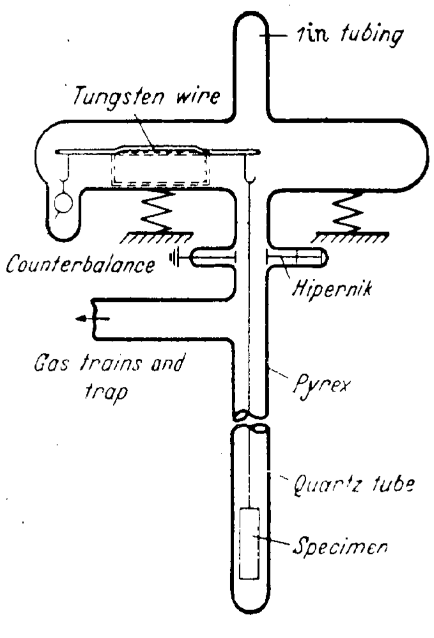

Fig.20 Microbalance System (Gulbransen[33]).

be followed by volumetric and manometric methods. Apparatus for such measurements is in principle quite simple. It consists of a reaction chamber, connected to a reservoir of the reacting gas. The reaction is followed by measuring the pressure drop in the system on by measuring the volume consumed. Apparatus used by Kubaschewski and others[34] is shown in figure 21.

ELECTROMETRIC METHOD

The electrometric method has been developed in particular to determine the thickness of thin films of oxidation products on metals. Hence this can be used to determine the rate of oxidation with time. The method consisted of determining the quantity of electricity needed to reduce the oxidation product either to metallic state or to a lower state of oxidation. Campbell and Thomas[35] have designed a electrolysis cell as shown in figure 22.

The film thickness, ξ, in Angstrom units is given by

$$\xi = \frac{It\,M \times 10^{5}}{2\,A \times 96500}$$

where I = Current in milliamperes

t = time in seconds

M = Weight in gms of oxidation product giving one g-atom of oxygen or equivalent on reduction.

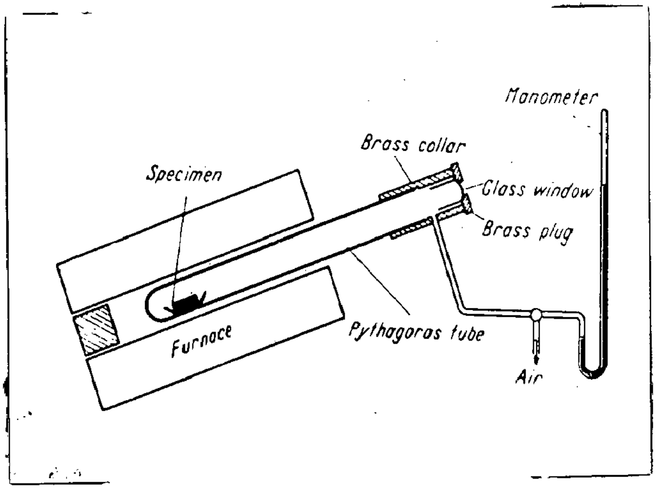

Fig.21 Manometric Equipment (Kubaschewski[34]).

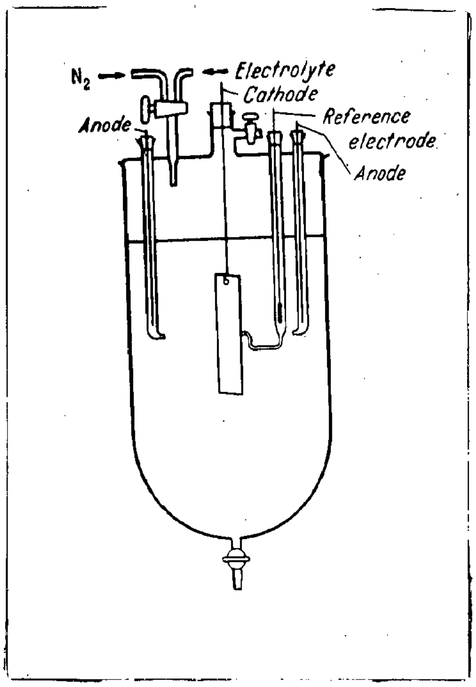

Fig.22 Electrolysis Cell (Campbell & Thomas[35])

ρ = Density of oxidation product.

A = Area in Cm^2.

ELECTRICAL RESISTANCE METHOD

In this method, the change in electrical resistance of a wire after heating for various times has been used to measure the decrease in cross-sectional area of the metal caused by oxidation. This method has been used by Pilling and Bedworth[4]. The method is only valid if the increase in resistance is entirely due to the decrease in cross-section.

CHAPTER-II

II

EXPERIMENTAL WORK

II.1. INTRODUCTION

In the present work an attempt has been made to study the kinetics of oxidation of Copper and the effect of various alloying additions on the oxidation kinetics of copper in air in the temperature range 500 - 900 °C. Alloys of different composition were prepared, analysed and then oxidized at different temperatures. Thermogravimetric technique has been employed to study the oxidation kinetics.

II-2. MATERIALS USED

The details of the materials used in this investigation are as follows:

MATERIAL	PURITY	NAME OF SUPPLIER
Electrolytic Copper	99.95%	Chempur Pvt.Ltd.Calcutta.
Aluminium	99.7%	Indian Standard Metal Co. Ltd. Bombay.
Zinc	99.9%	Indian Standard Metal Co. Ltd.Bombay.
Cadmium	99.95%	Chempur Pvt.Ltd.Calcutta
Silicon	99.9%	'Do'
Tin	99.95%	Indian Standard Metal Co. Bombay.
Manganese	99.95%	Indian Standard Metal Co. Ltd. Bombay.

II-3. ALLOY PREPARATION

The alloys were prepared by melting electrolytic Copper under charcoal in a graphite crucible in forced draught pit furnace and adding the calculated amount of alloying element. The bars of 2 Cm dia were cast in metallic steel moulds and then machined to a smooth finish.

Specimens were cut from these bars. The various alloys were then analyzed. Table 3 gives the composition of the alloys prepared:

TABLE 3

ELEMENT	ALLOY CONTENT		COPPER %
	NOMINAL %	ACTUAL %	
ALUMINIUM	2	2.10	97.85
	4	3.95	96.00
	7	7.12	92.83
ZINC	7	6.4	93.55
	15	14.7	85.25
	20	18.8	81.15
	30	31.0	68.95
	40	38.0	61.85
SILICON	2.5	3.0	96.95
	7.0	7.1	92.85
TIN	7.0	7.14	92.81
MANGANESE	7.0	7.10	92.85
CADMIUM	7.0	6.82	93.13

II-4. DETAILS OF EXPERIMENTAL SET-UP USED

The schematic assembly of the set-up used for the present investigation is shown in figure 23. The assembly mainly consists of a balance and a furnace.

BALANCE

The balance used was a Single- Pan Analytical Balance owa labor type 707.04, specially modified so that the specimen can be suspended by a thin wire (Nichrome wire of 36 gauge) from the pan of the balance as shown in figure 23. The balance was one of the aperiodic projection type, reading upto 100 mg on the illuminated scale to a sensitivity of 0.1 mg.

The zero of the balance was checked at intervals during the test by bringing the beam to rest and transferring the specimen suspension to a another hook provided nearby.

FURNACE

The furnace tube was of Alumina , 2 inch bore and 3 ft long. The winding was done by Kanthal wire of 18 gauge. The resistance of the furnace was 25 ohms. The alumina tube was then kept in a cylindrical steel shell of dimensions 18" dia and 24" length and the space between the tube and the outer shell of the furnace was then packed with asbestos

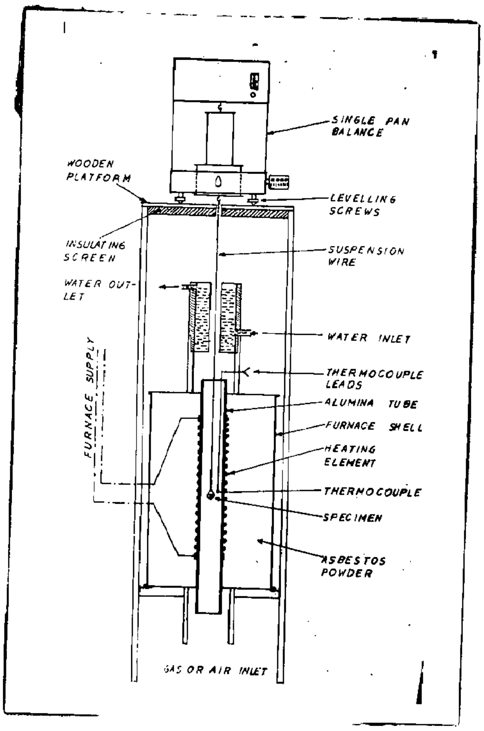

Fig.23 Schematic Diagram of Experimental Set Up.

powder. The ends of the shell were then closed by nuts and bolts.

The temperature of the furnace was measured by a Pt-Pt/13%Rh thermocouple inserted into the furnace tube from the top end, bare end of the thermocouple was 1/4 inch above the upper end of the specimen and about ½" away from the centre line of the alumina tube. The temperature control was maintained to ± $5^{o}C$ over a 6 inch central zone by means of a energy regulator (Sunvick Range 0 to 100). Thermocouple wires were connected through lead wires to a Pt-Pt/13% Rh temperature indicator.

In order to minimize the effect of the heat from the furnace on the balance, arrangements were made for water-cooling just above the top end of the tube and by inserting an insulating screen. The hole through which the wire passes was just sufficient to give the wire free movement. The space between the furnace and the balance was properly covered to proteat the wire from being deflected by air currents.

II.5. PROCEDURE

A nichrome wire of about 2 ft. length, having a nichrome cage at one end was introduced from the top of the furnace. The wire was then lowered so that the

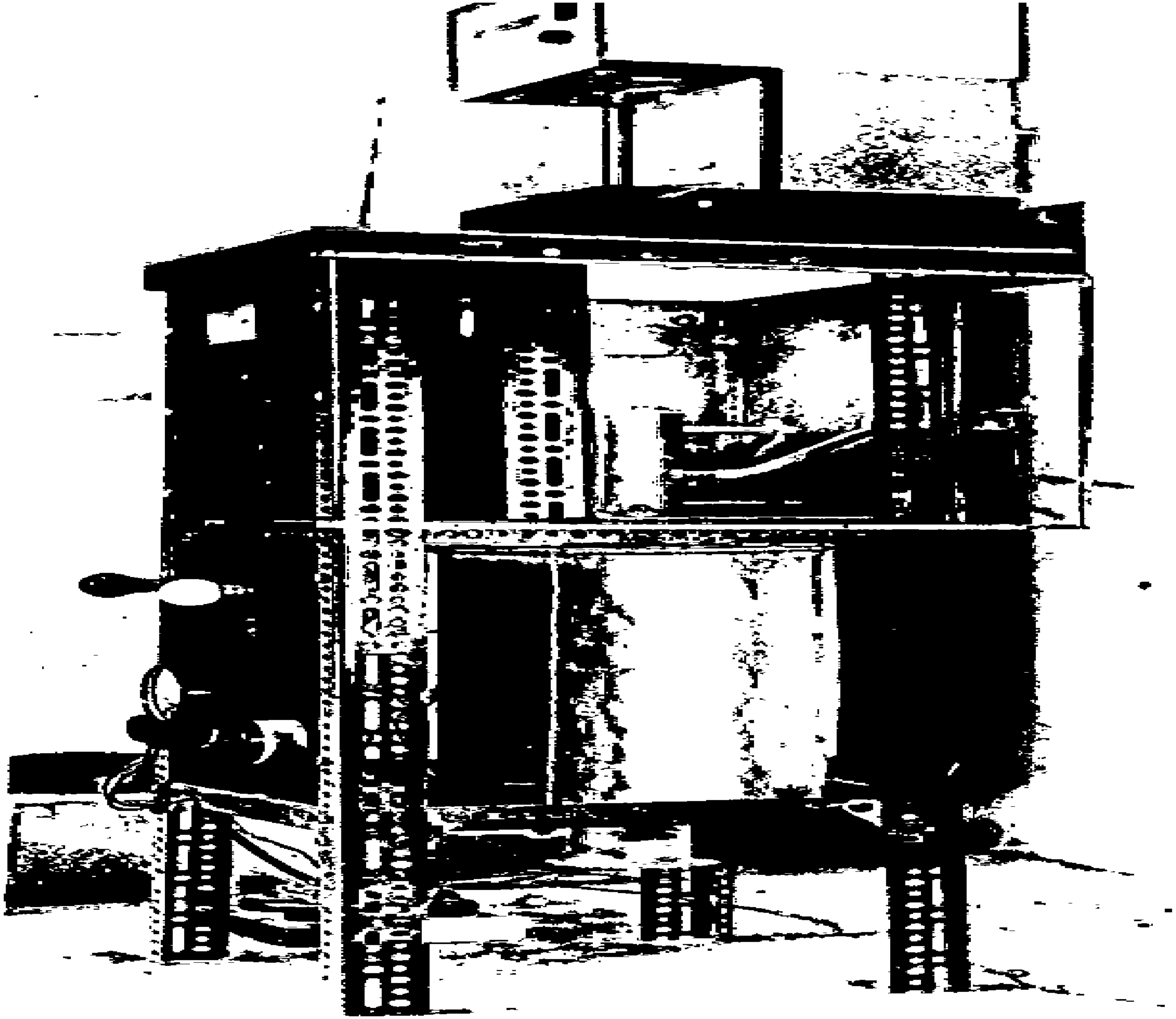

Fig.24 General view of the Experimental set up

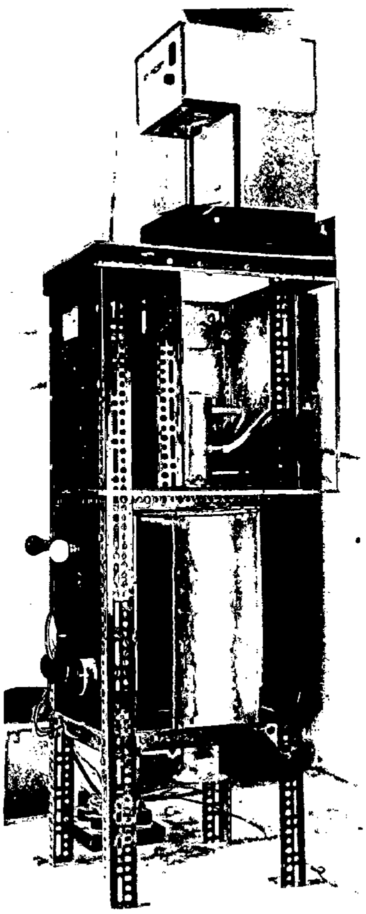

Fig.24 G set up

cage comes out of the furnace bottom. The specimen properly cleaned, was then kept in the cage. The furnace was then switched on and when the furnace reached the required temperature of oxidation, the wire holding the cage with specimen was lifted upwards and the top end of the wire was then connected to a hook at the bottom of the pan of the balance.

Weight measurements were made at fixed intervals and the increase in weight with time was noted for the determination of the oxidation rate.

The experiments were then conducted at various temperatures ranging from 500 to 900 °C.

This method of direct weighing while the specimen is at temperature, avoids difficulties due to exfoliation of the scale during cooling, and to changes in weight of the scale after cooling.

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CHAPTER-III

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III

RESULTS AND DISCUSSION

In this chapter the results of the present investigation are summarized in first part and it is followed by a brief discussion in the second part.

III.1. RESULTS

The oxidation data for pure Copper and its alloys obtained from the experiments are summarized in tables I to VII (Appendix). From these data the curves have been plotted as shown in figures 25 to 38. To check the validity of the parabolic law during oxidation , the square of the weight gain per unit area vs time curves have been plotted in figures 39 to 42. In cases where the parabolic law is not obeyed, the weight gain has been plotted against the logarithm of time (figure 43 to 50). Figure 51 shows the Arrheneius plot for the oxidation of Copper in air.= Figure 52 and 53 represents the effect of Zinc content on the oxidation of pure Copper and the effect of temperature on the oxidation of Copper- Aluminium alloys respectively.

The comparative effect of same amount (7 wt.%) of various additives (Zinc , Aluminium, Silicon,Tin, Manganese and Cadmium) on the oxidation of Copper at 700°C has been represented in figure 55.

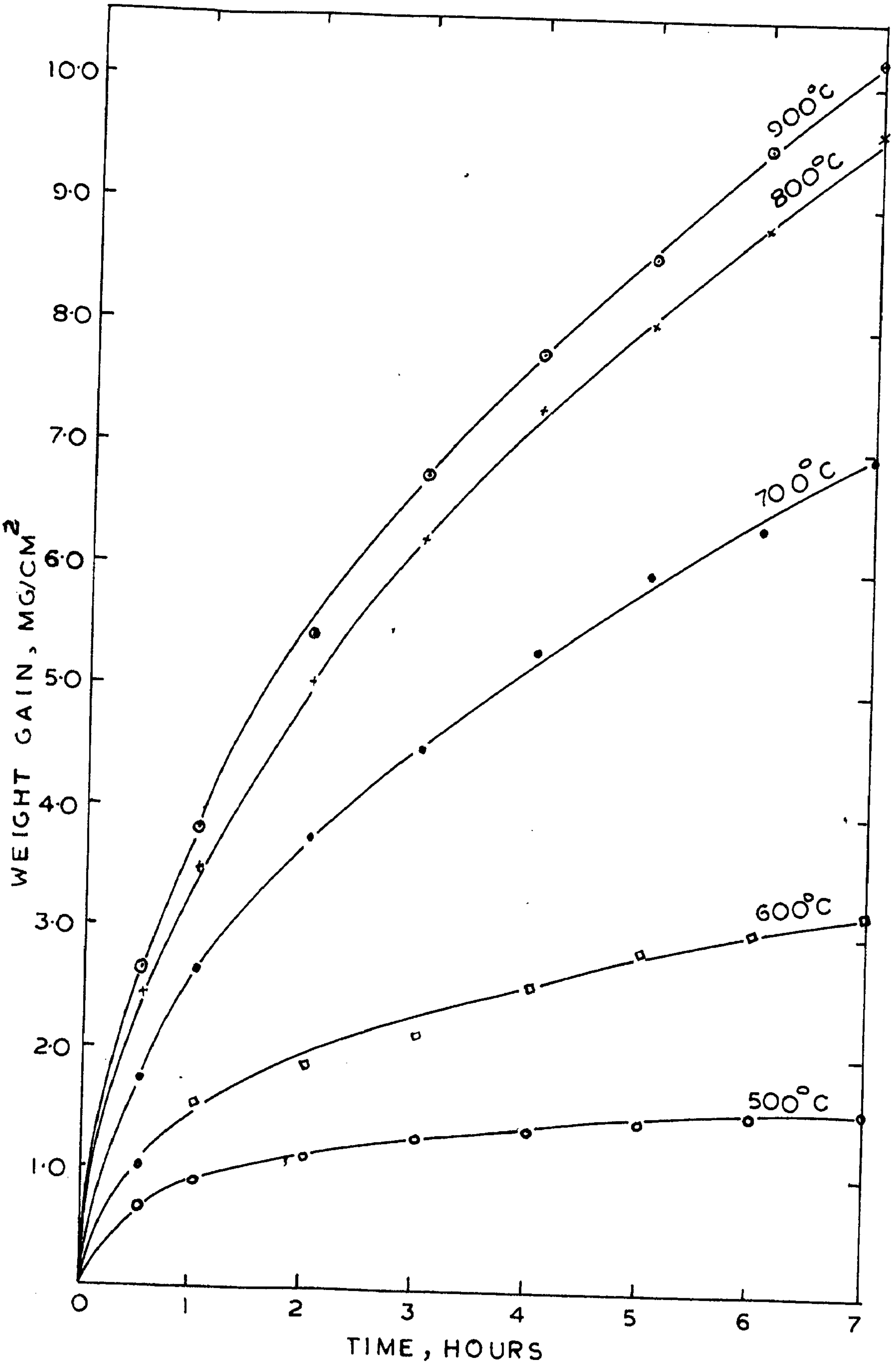


FIG.25.WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF PURE COPPER AT VARIOUS TEMPERATURES.

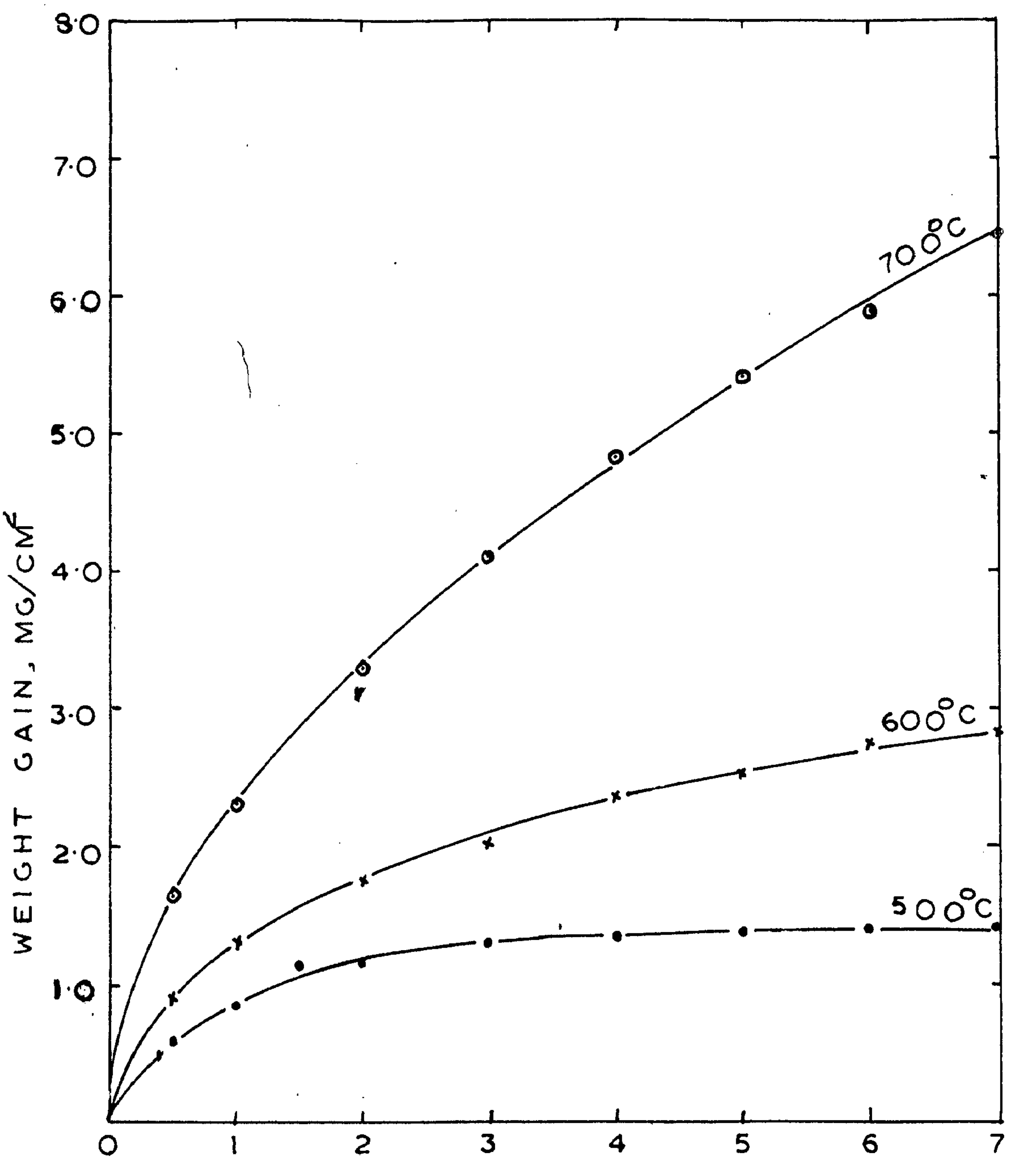


FIG26. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-7%ZINC ALLOY AT VARIOUS TEMPERATURES

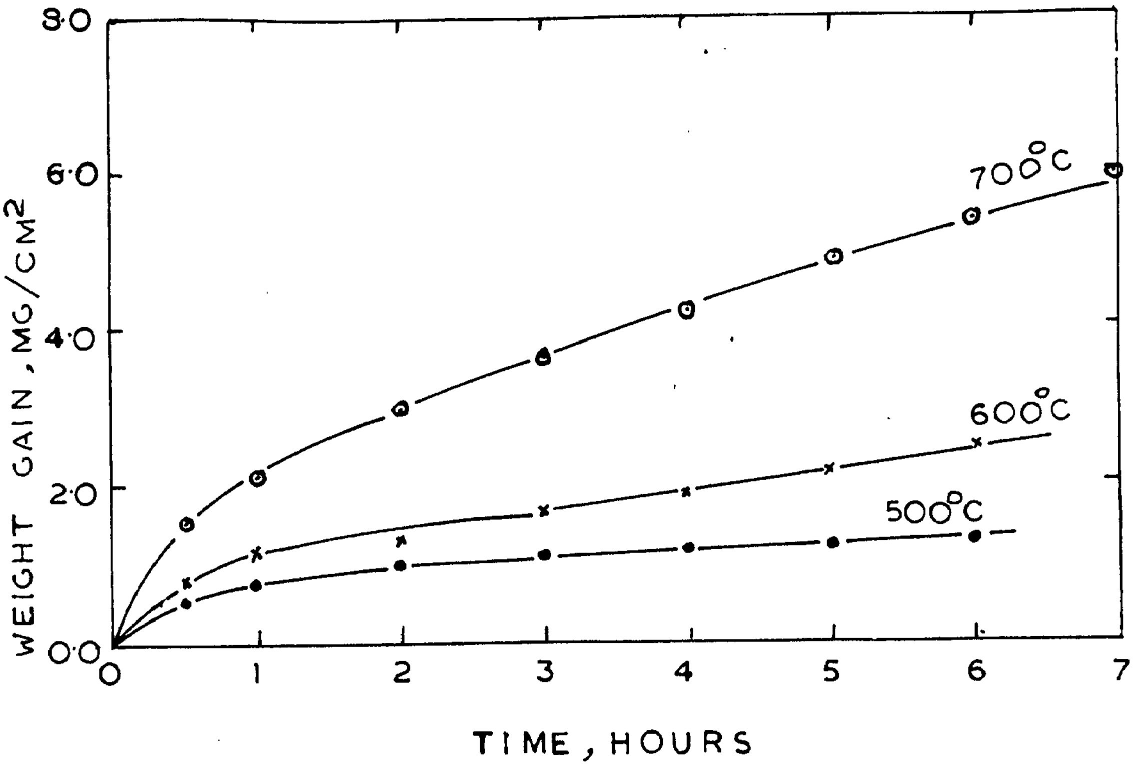


FIG.27.WEIGHT GAIN VS TIME PLOT FOR OXIDATION OF COPPER-15%ZINC ALLOYS

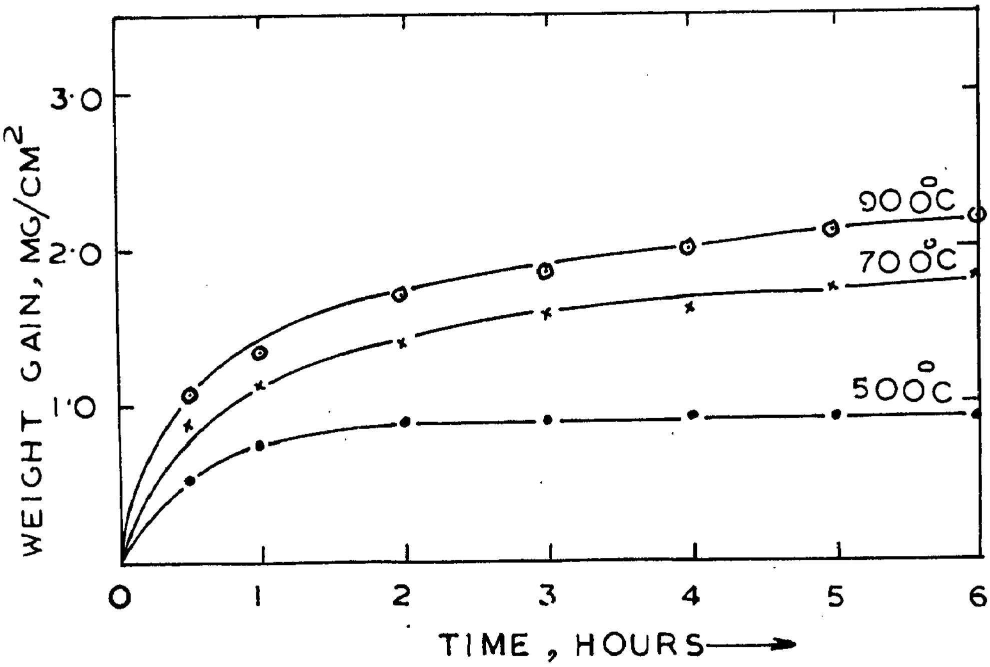


FIG28.WEIGHT GAIN VS TIME PLOT FOR OXIDATION OF COPPER-20%ZINC ALLOYS

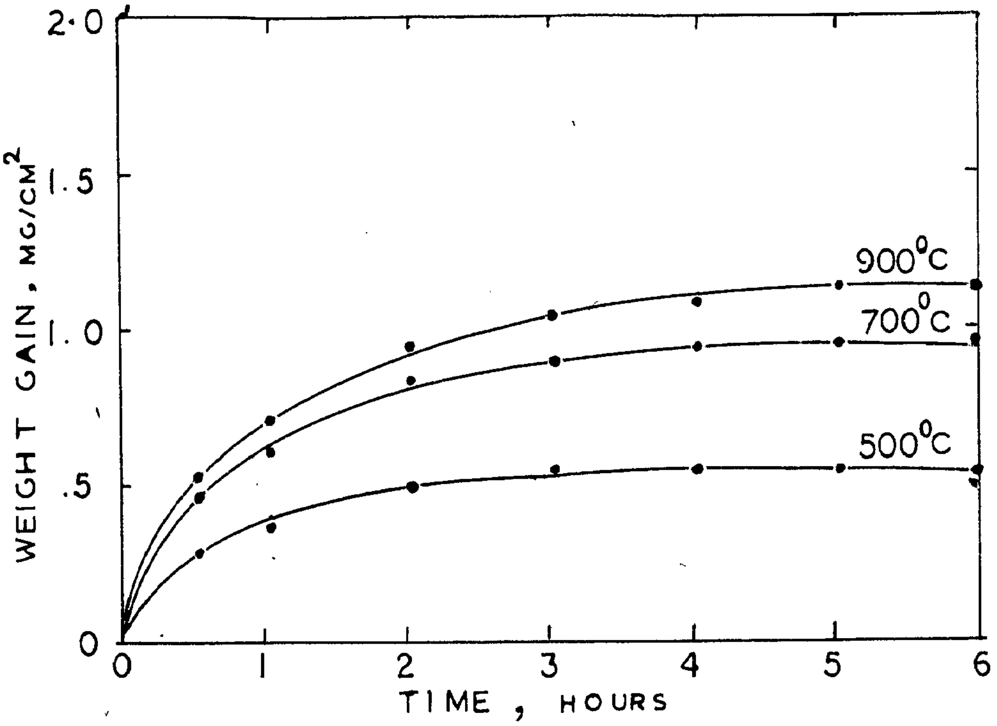


FIG:29. WEIGHT GAIN VS TIME PLOT FOR OXIDATION OF COPPER-30%ZINC AT VARIOUS TEMPERATURES

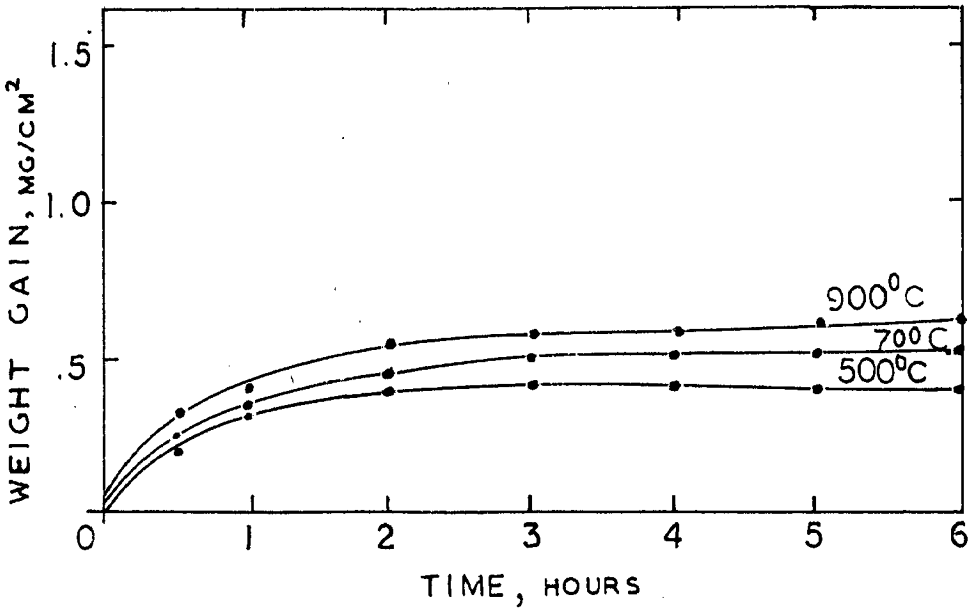


FIG:30. WEIGHT GAIN VS TIME PLOT FOR OXIDATION OF COPPER-40%ZINC AT VARIOUS TEMPERATURES

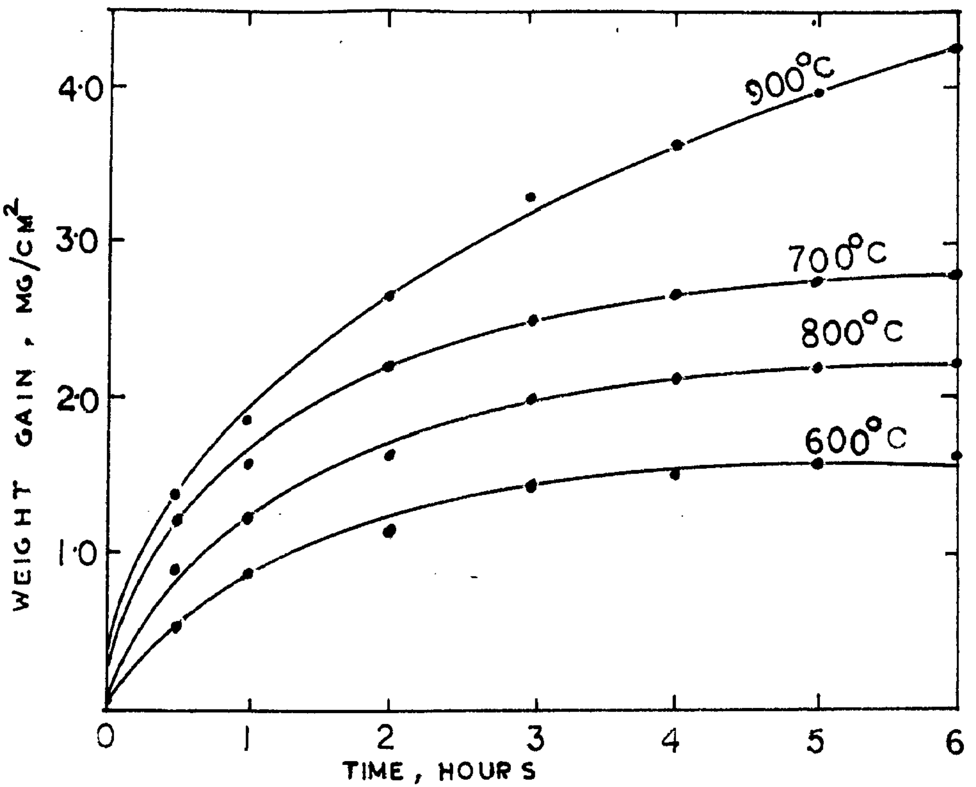


FIG:31. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-2 %ALUMINIUM ALLOY

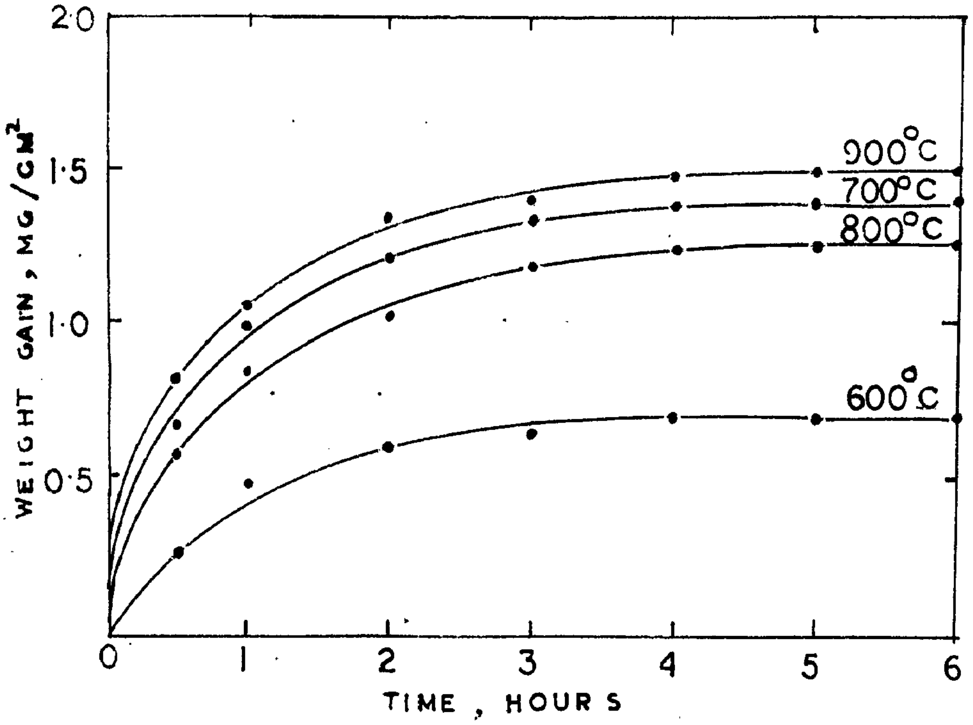


FIG.32. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-4 %ALUMINIUM ALLOY

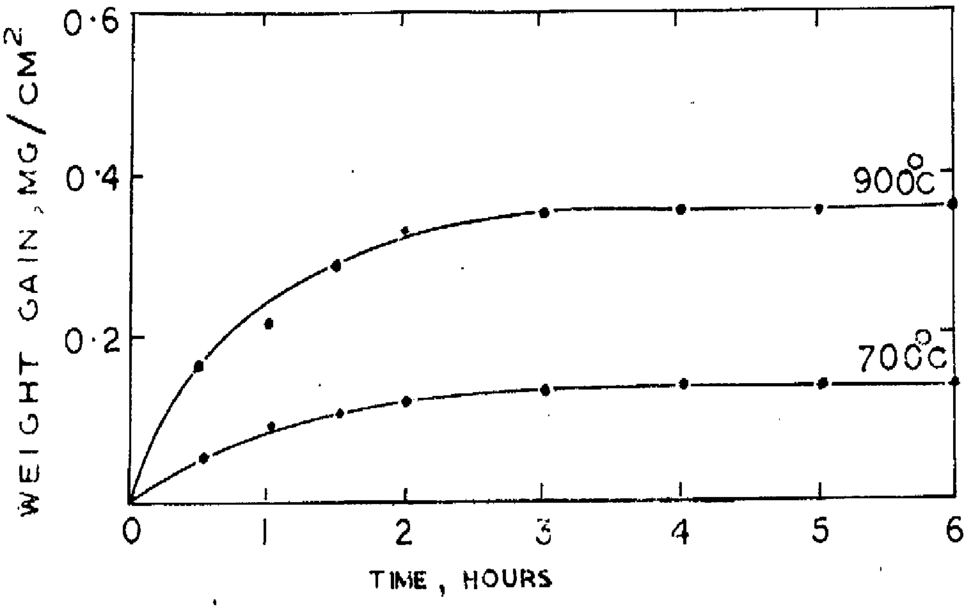


FIG.33. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-7%ALUMINIUM ALLOY

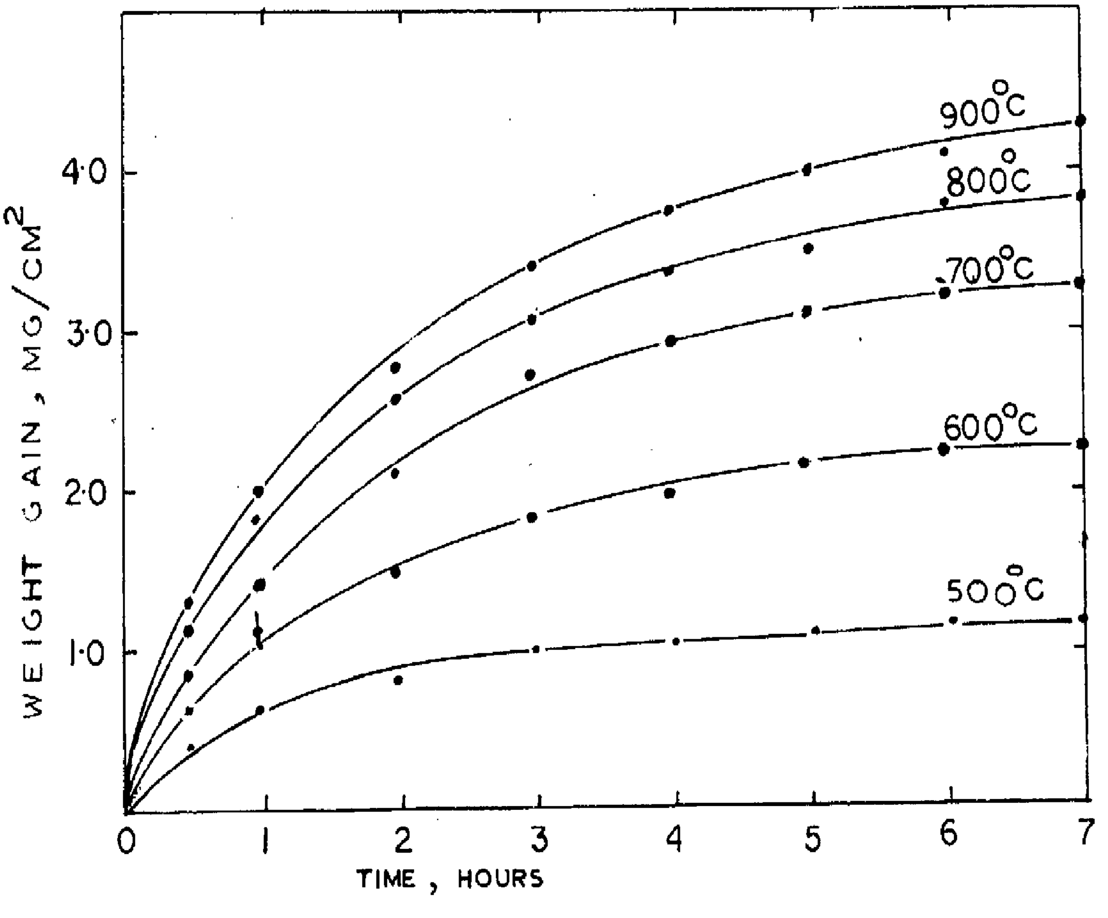


FIG.34WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION

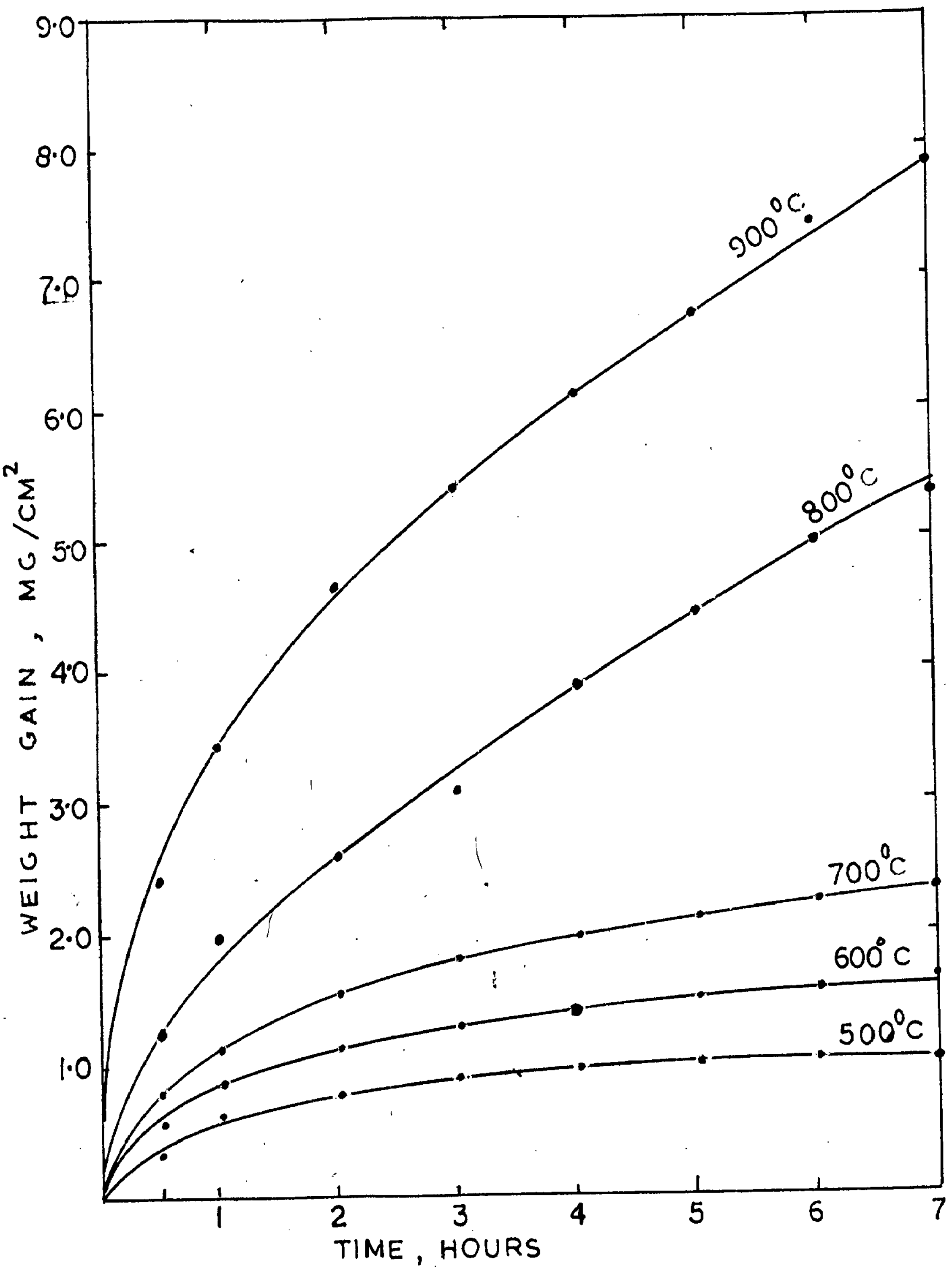


FIG.35. WEIGHT GAIN VS. TIME PLOT FOR THE OXIDATION OF COPPER-3% SILICON AT VARIOUS TEMPERATURES.

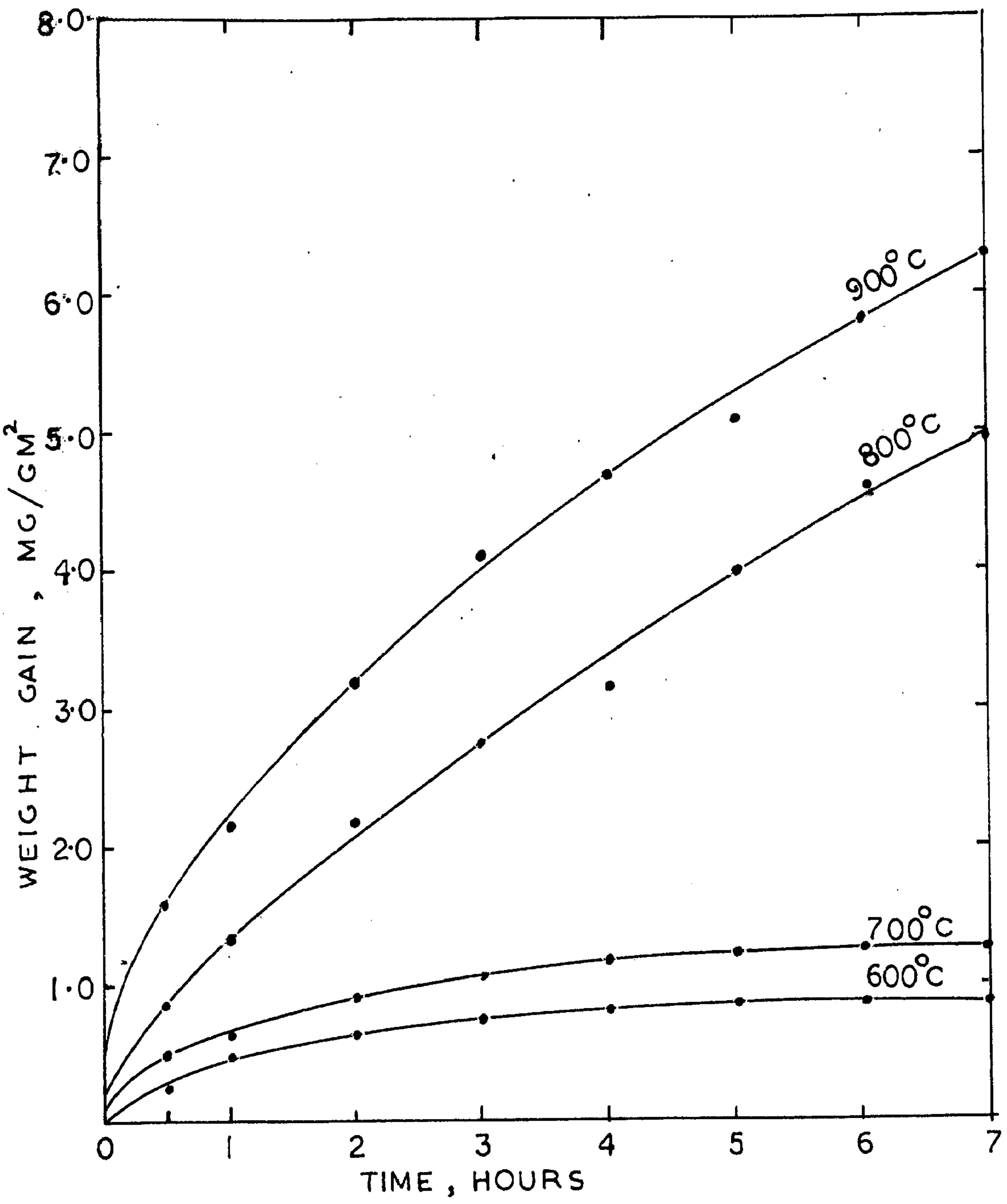


FIG36. WEIGHT GAIN VS. TIME PLOT FOR THE OXIDATION OF COPPER-7% SILICON AT VARIOUS TEMPERATURES.

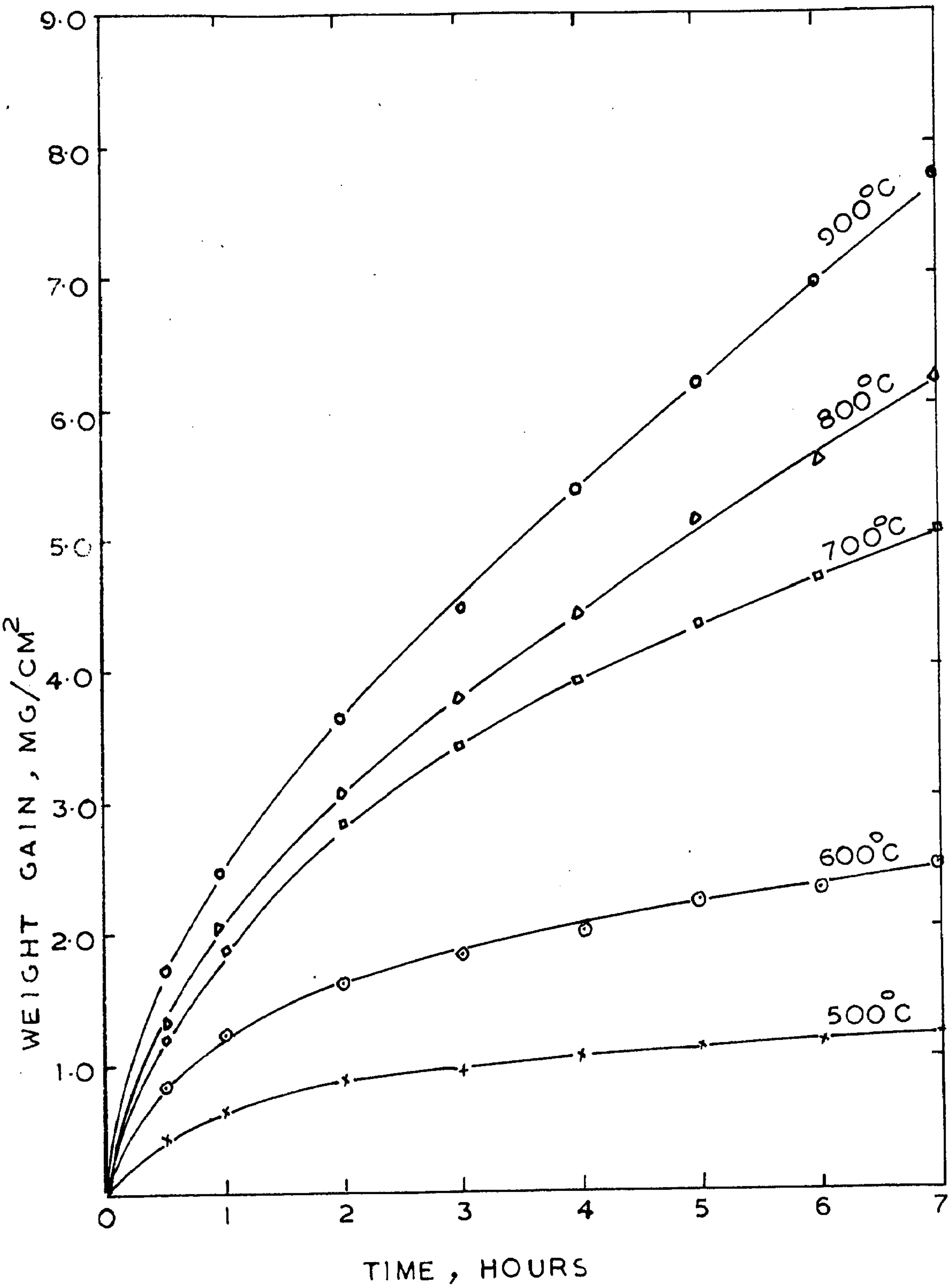


FIG37. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-7%MANGANESE ALLOY

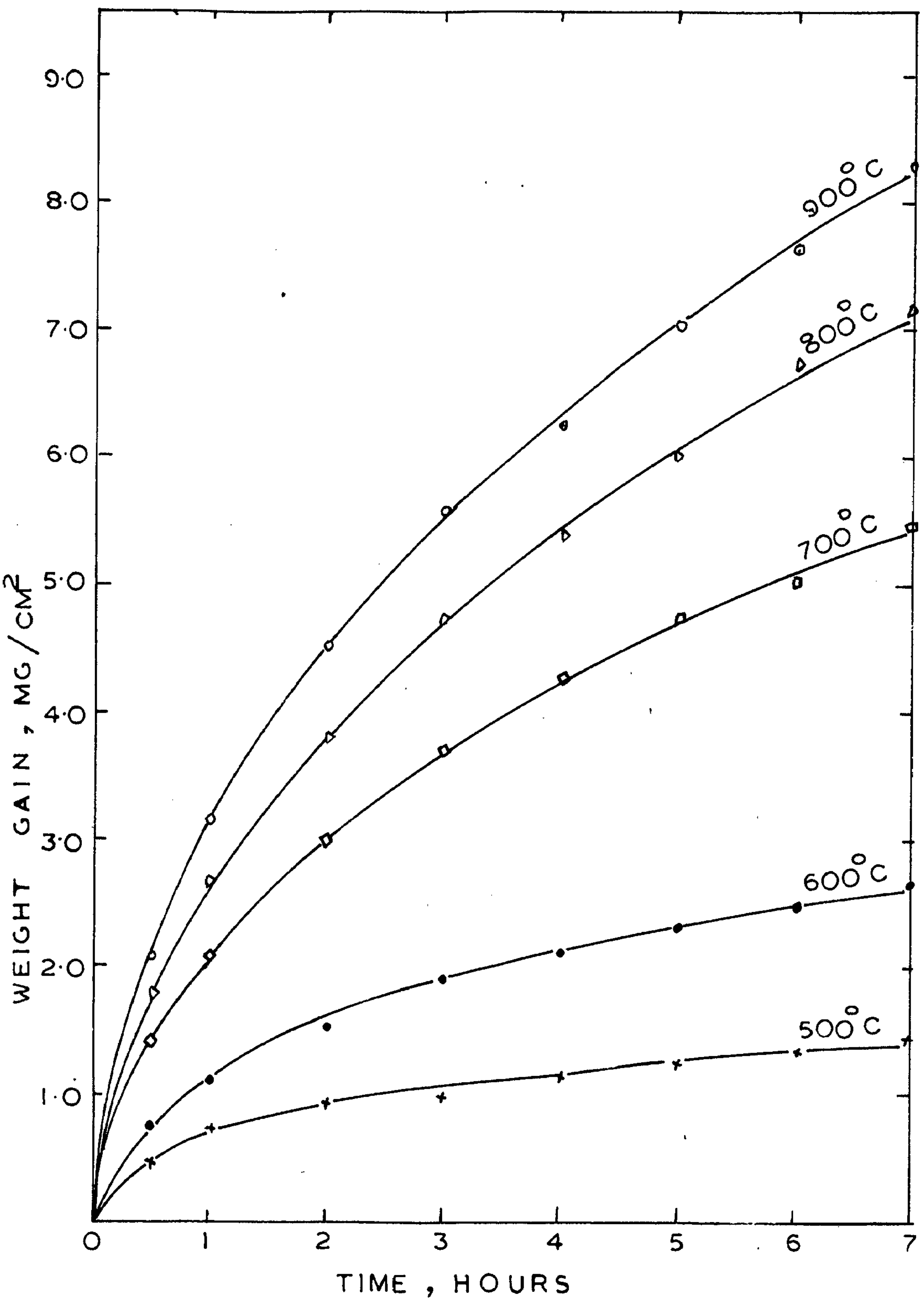
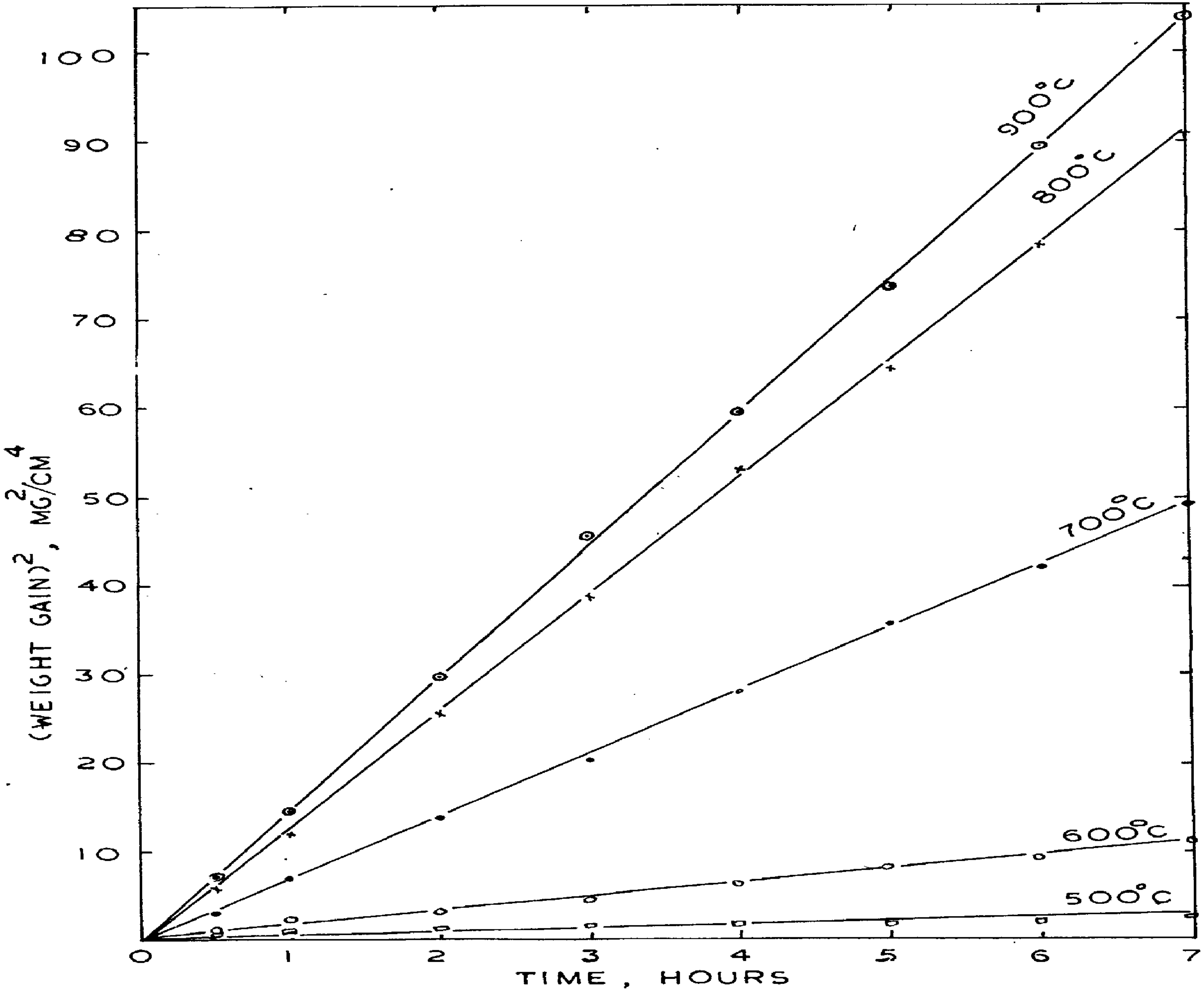
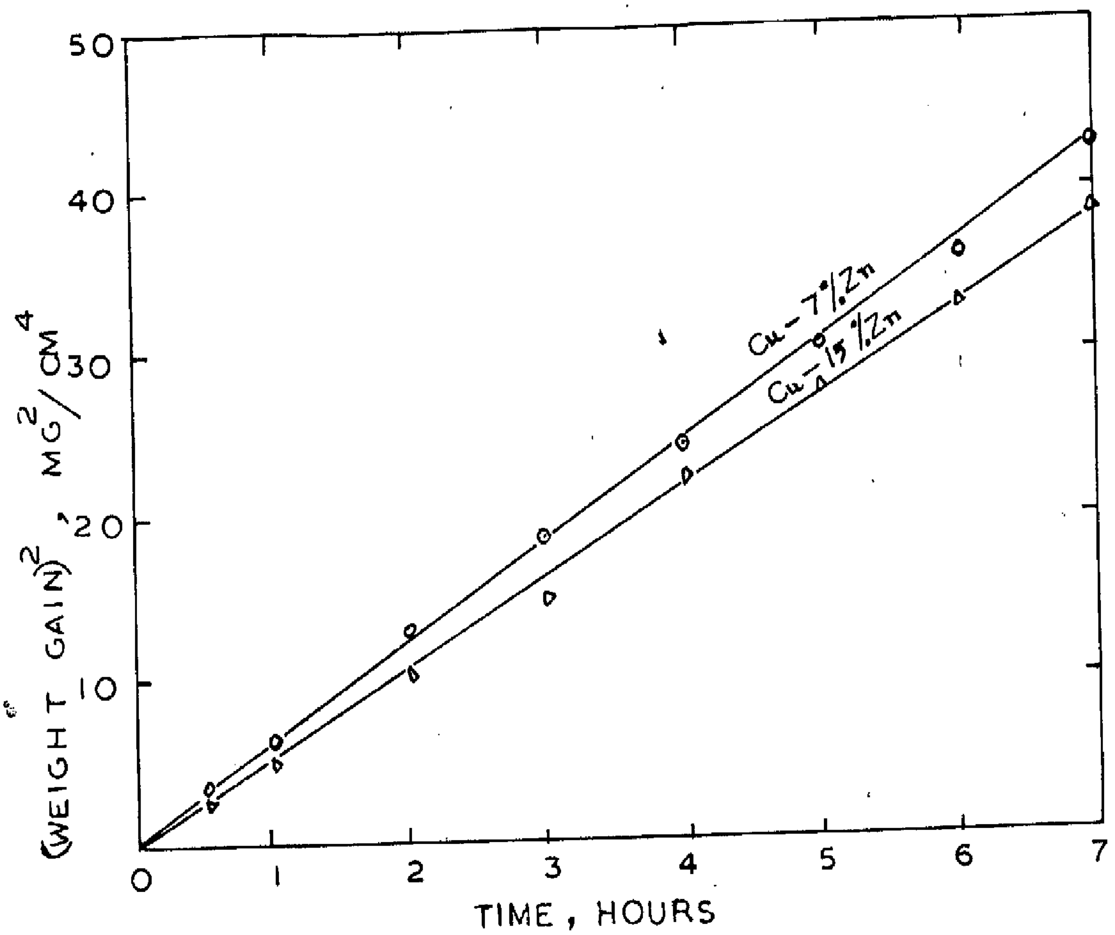
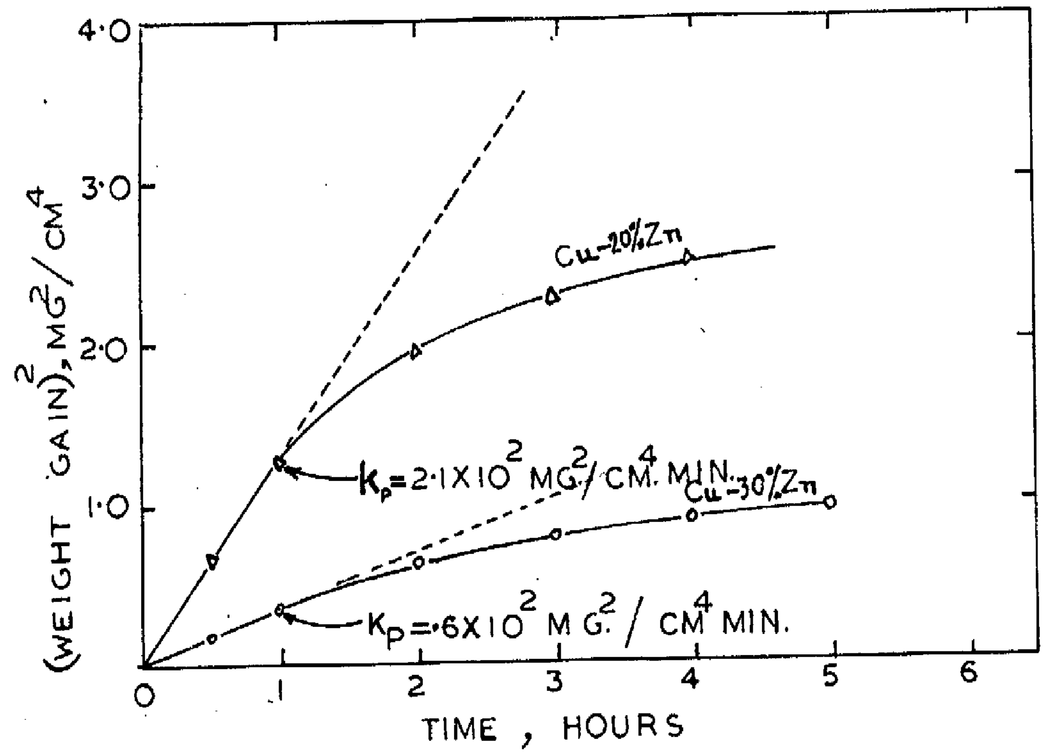


FIG38. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER—7%CADMIUM ALLOY


(WEIGHT GAIN)^2, MG^2/CM^4
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
TIME, HOURS
900°C
800°C
700°C
600°C
500°C


(WEIGHT GAIN)^2, MG^2/CM^4
50
40
30
20
10
0
1
2
3
4
5
6
7
TIME, HOURS
Cu-7%Zn
Cu-15%Zn

(a)


(WEIGHT GAIN)^2, MG^2/CM^4
4·0
3·0
2·0
1·0
0
1
2
3
4
5
6
TIME, HOURS
Cu-20%Zn
Cu-30%Zn
$K_p = 2{\cdot}1 \times 10^2$ MG^2/CM^4 MIN.
$K_p = {\cdot}6 \times 10^2$ MG^2/CM^4 MIN.

(b)

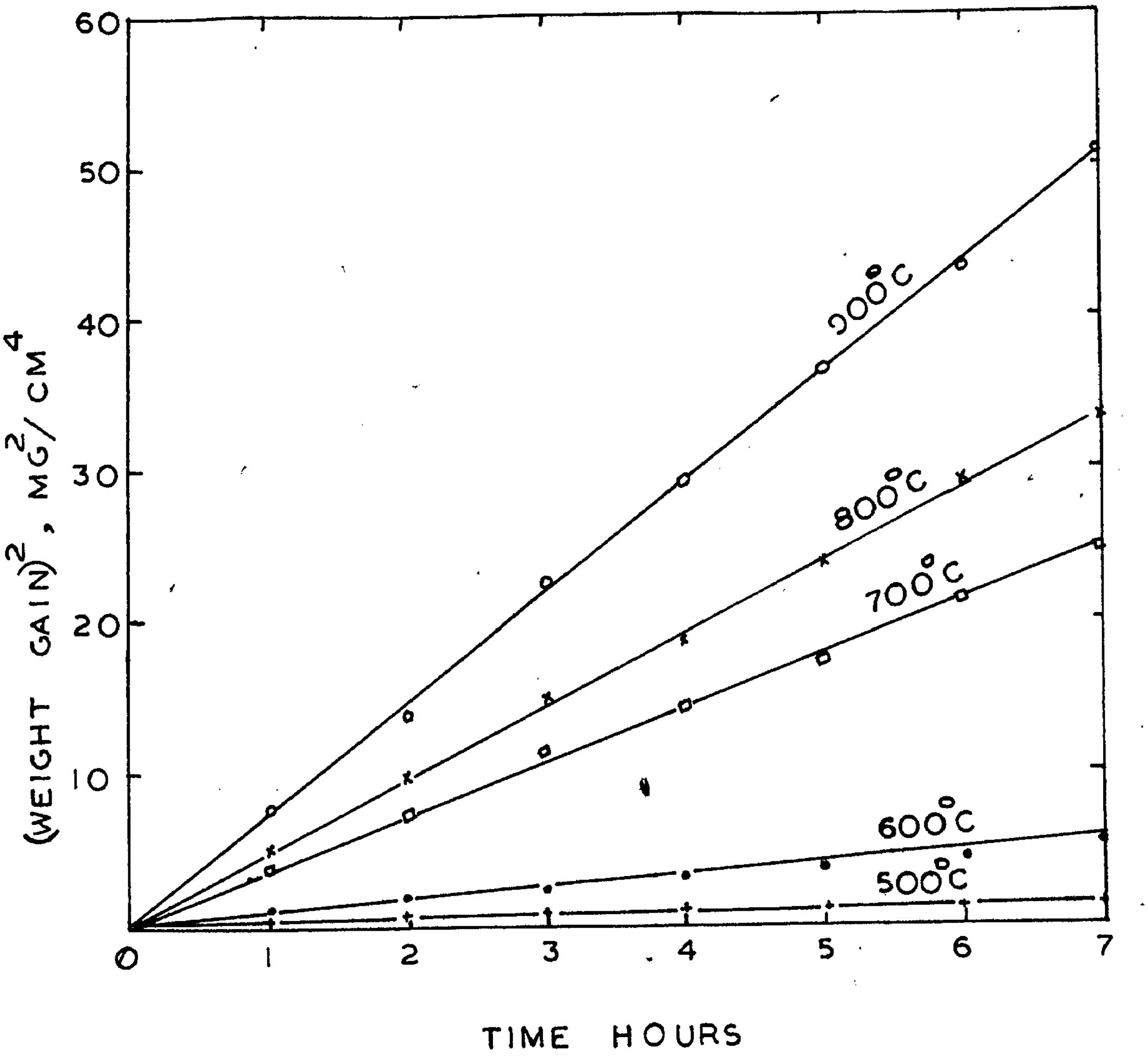


FIG.41. PARABOLIC PLOT FOR THE OXIDATION OF
COPPER- 7%MANGANESE ALLOY.

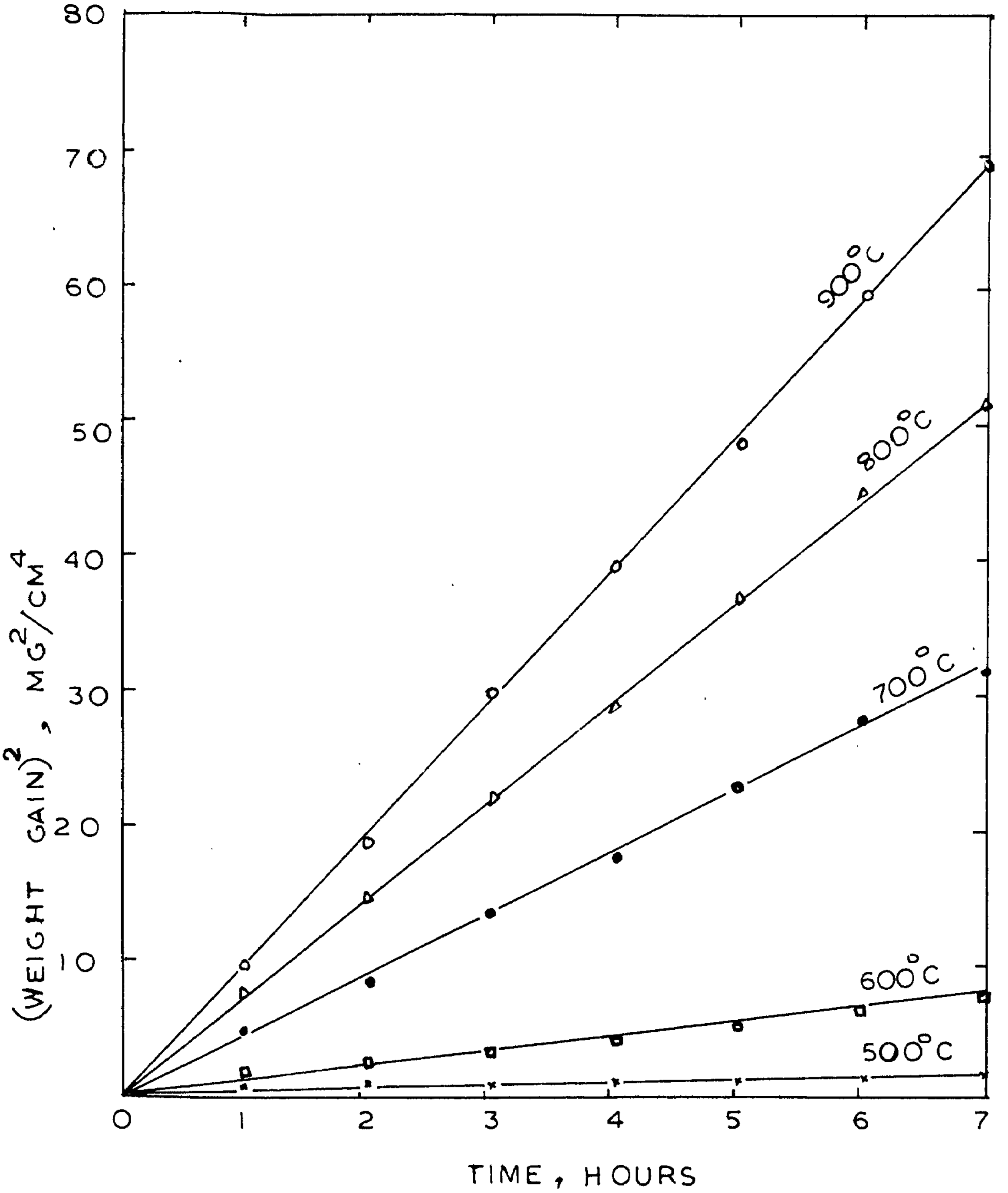


FIG 42. PARABOLIC PLOT FOR THE OXIDATION OF COPPER– 7 %CADMIUM ALLOY AT VARIOUS TEMPERATURES

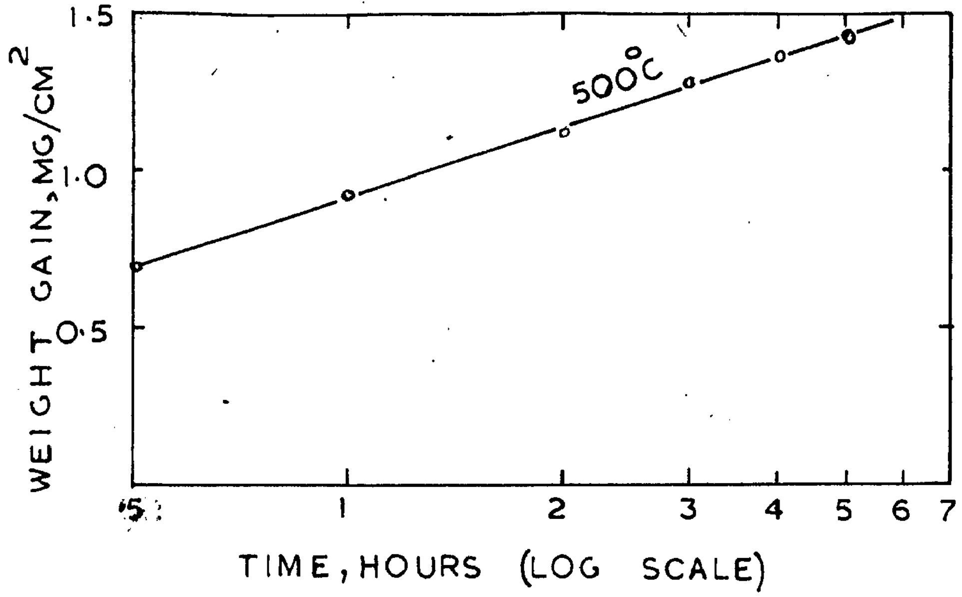


FIG 43. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER AT 500°C.

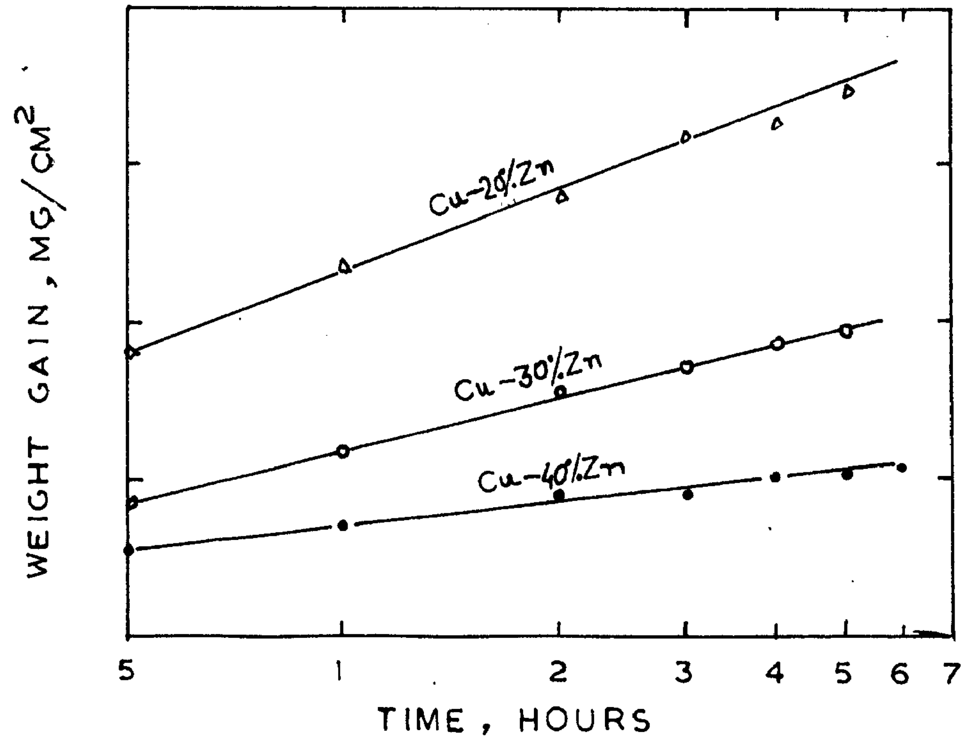


FIG44.WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER–ZINC ALLOYS AT 700°C

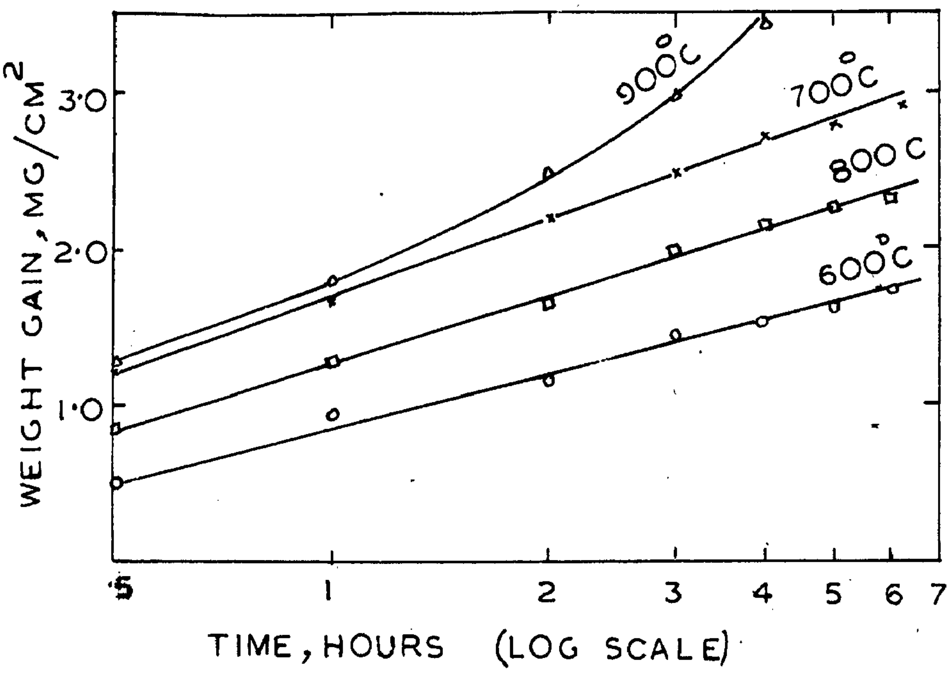


FIG45. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-2% ALUMINIUM ALLOY

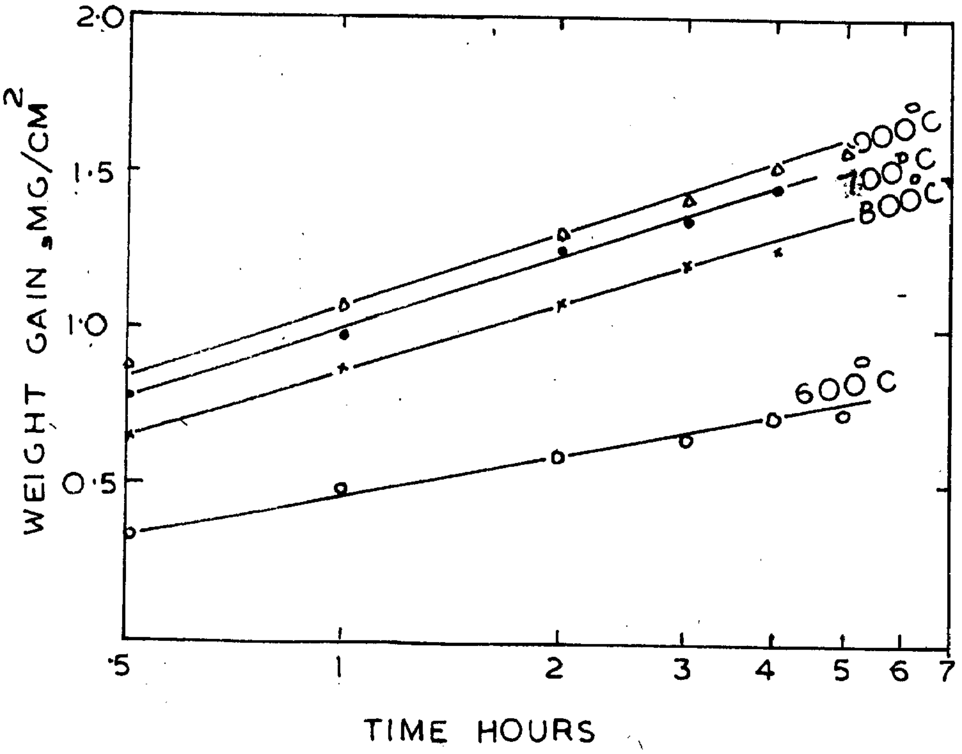


FIG46. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-4% ALLUMINIUM ALLOY

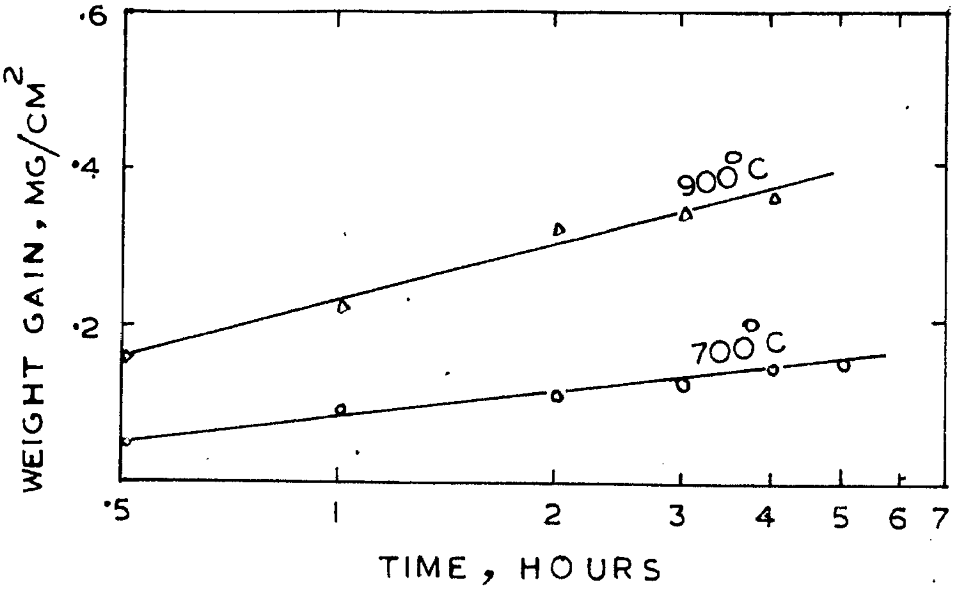


FIG47. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-7%ALUMINIUM ALLOY

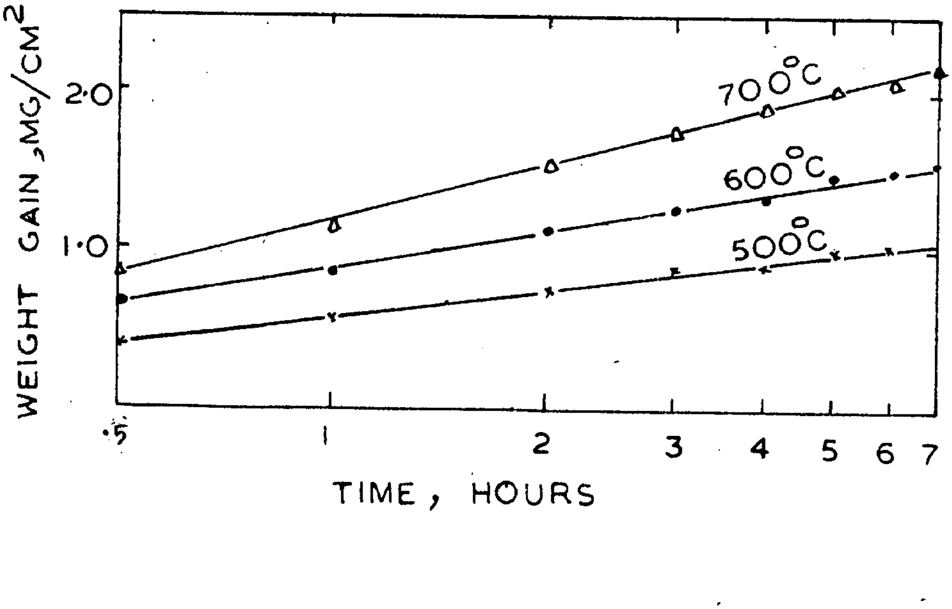


FIG48. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER-3 %SILICON ALLOY

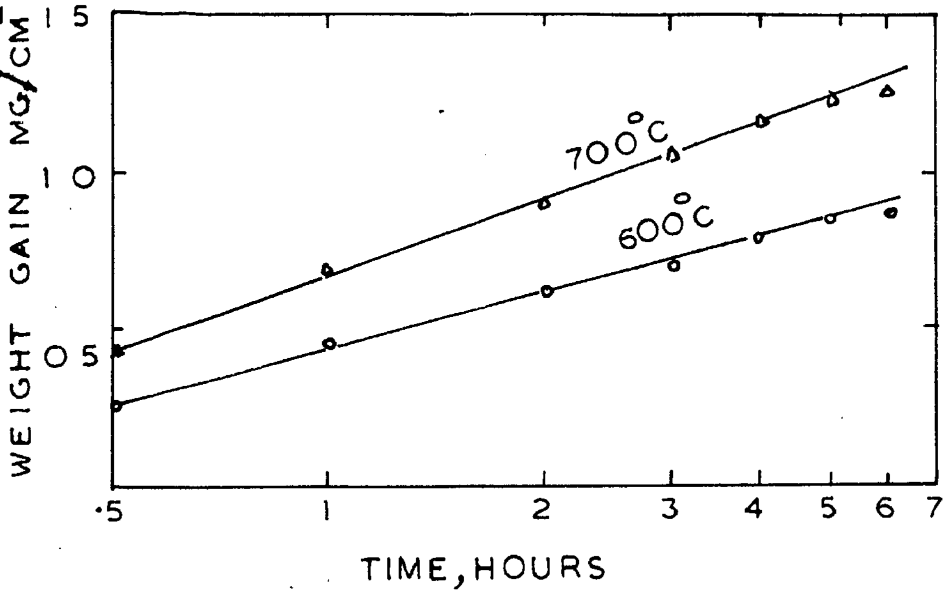


FIG49. WEIGHT GAIN VS TIME PLOT FOR THE OXIDATION OF COPPER—7 %SILICON ALLOY

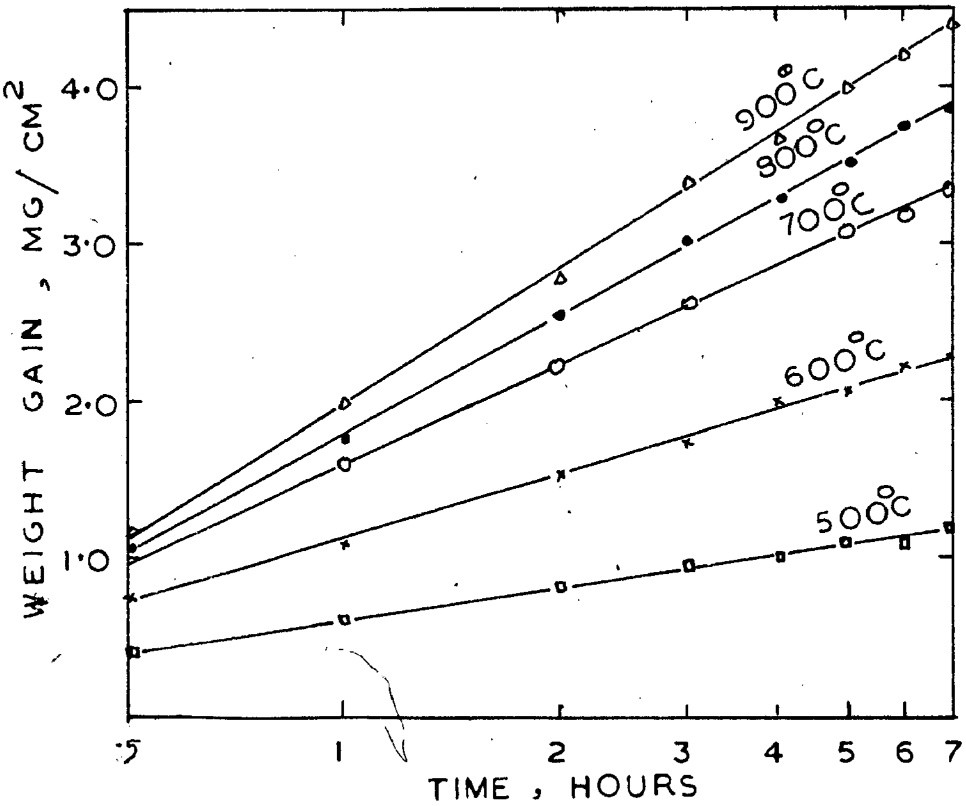


FIG50. WEIGHT GAIN VS TIME PLOT FOR OXIDATION OF COPPER—7 %TIN ALLOY

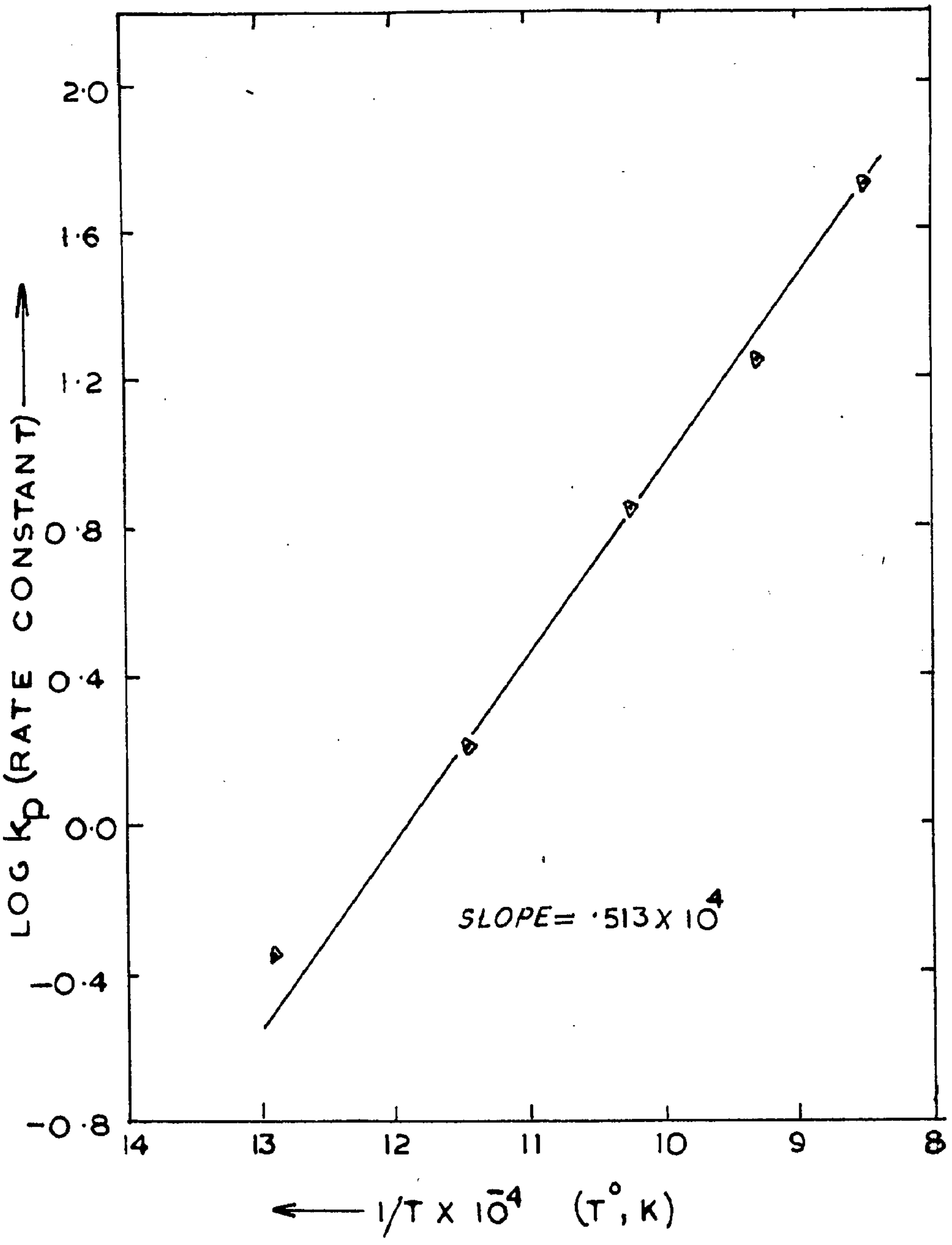


FIG 51. ARRHENIUS PLOT FOR THE OXIDATION OF COPPER.

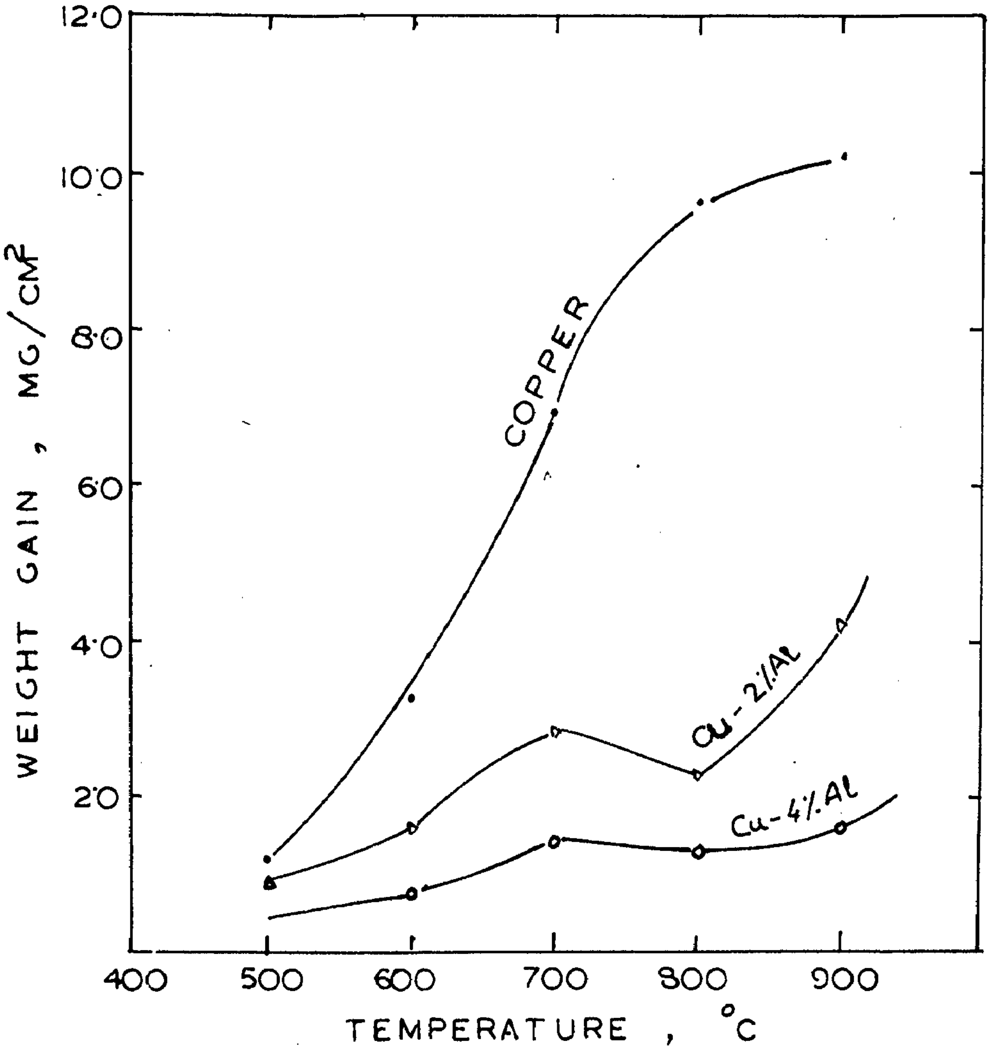


FIG53. WEIGHT GAIN IN 7-HOURS OF OXIDATION OF COPPER AND COPPER-ALUMINIUM ALLOYS AT DIFFERENT TEMPERATURES

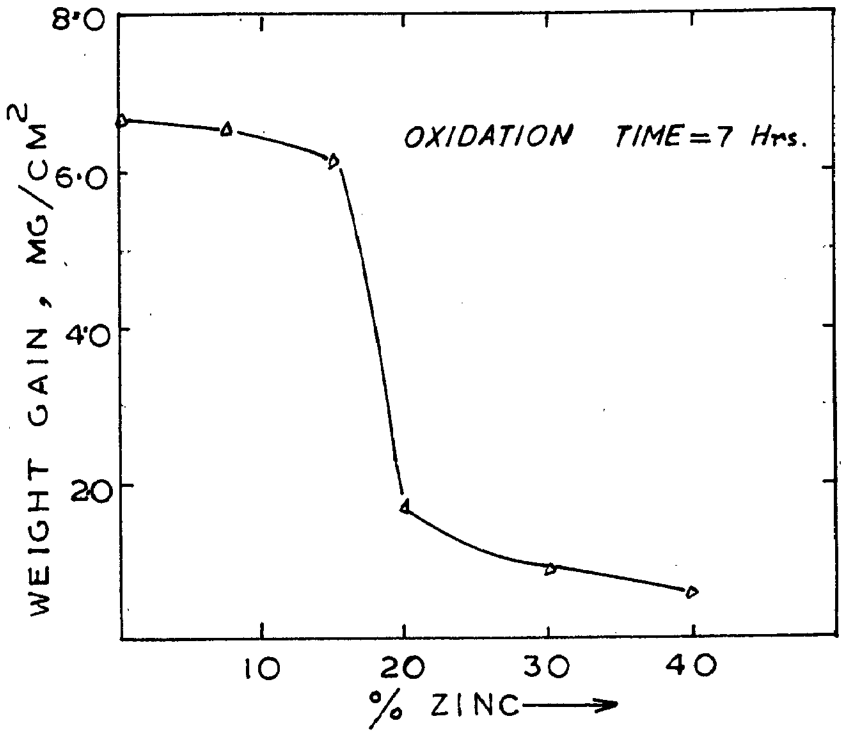


FIG.52. EFFECT OF THE AMOUNT OF ZINC ON THE OXIDATION OF COPPER AT 700°C.

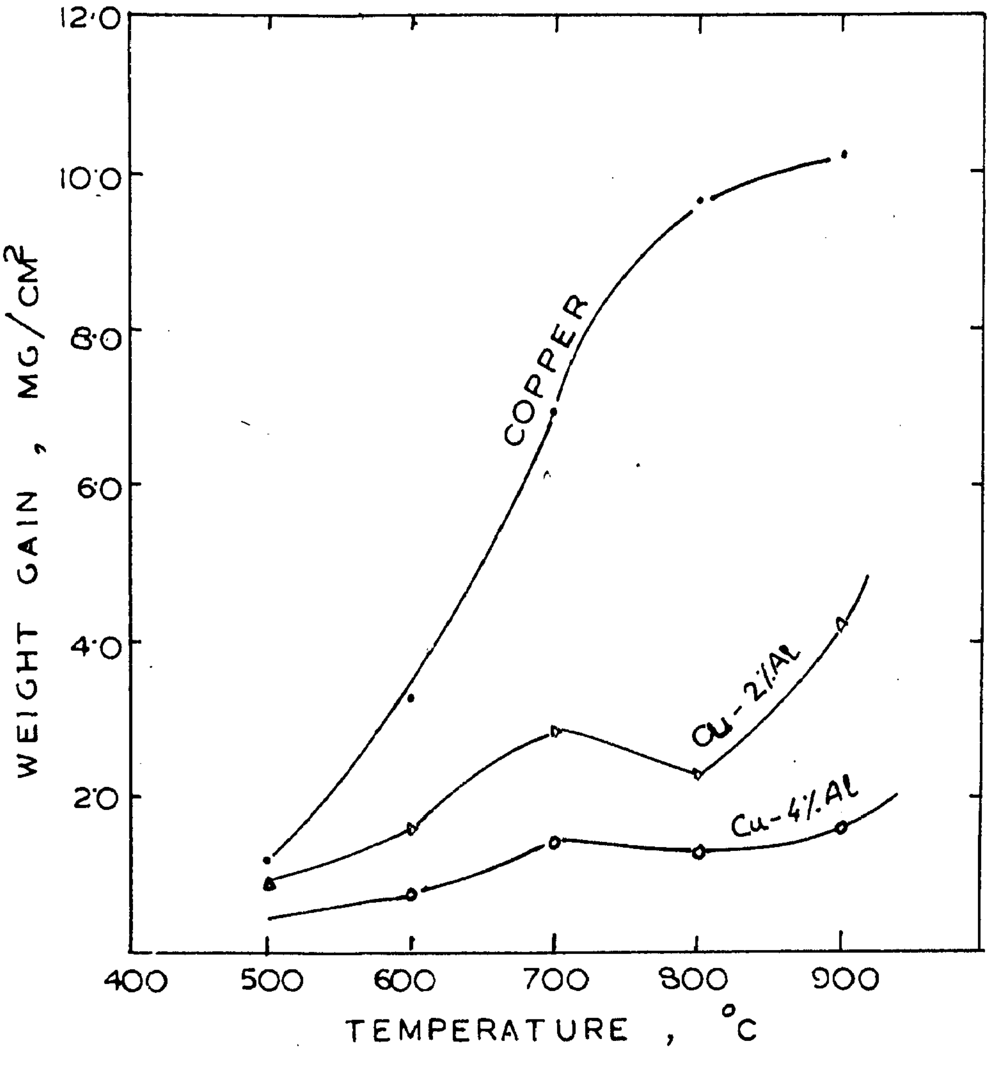


FIG53. WEIGHT GAIN IN 7-HOURS OF OXIDATION OF COPPER AND COPPER-ALUMINIUM ALLOYS AT DIFFERENT TEMPERATURES

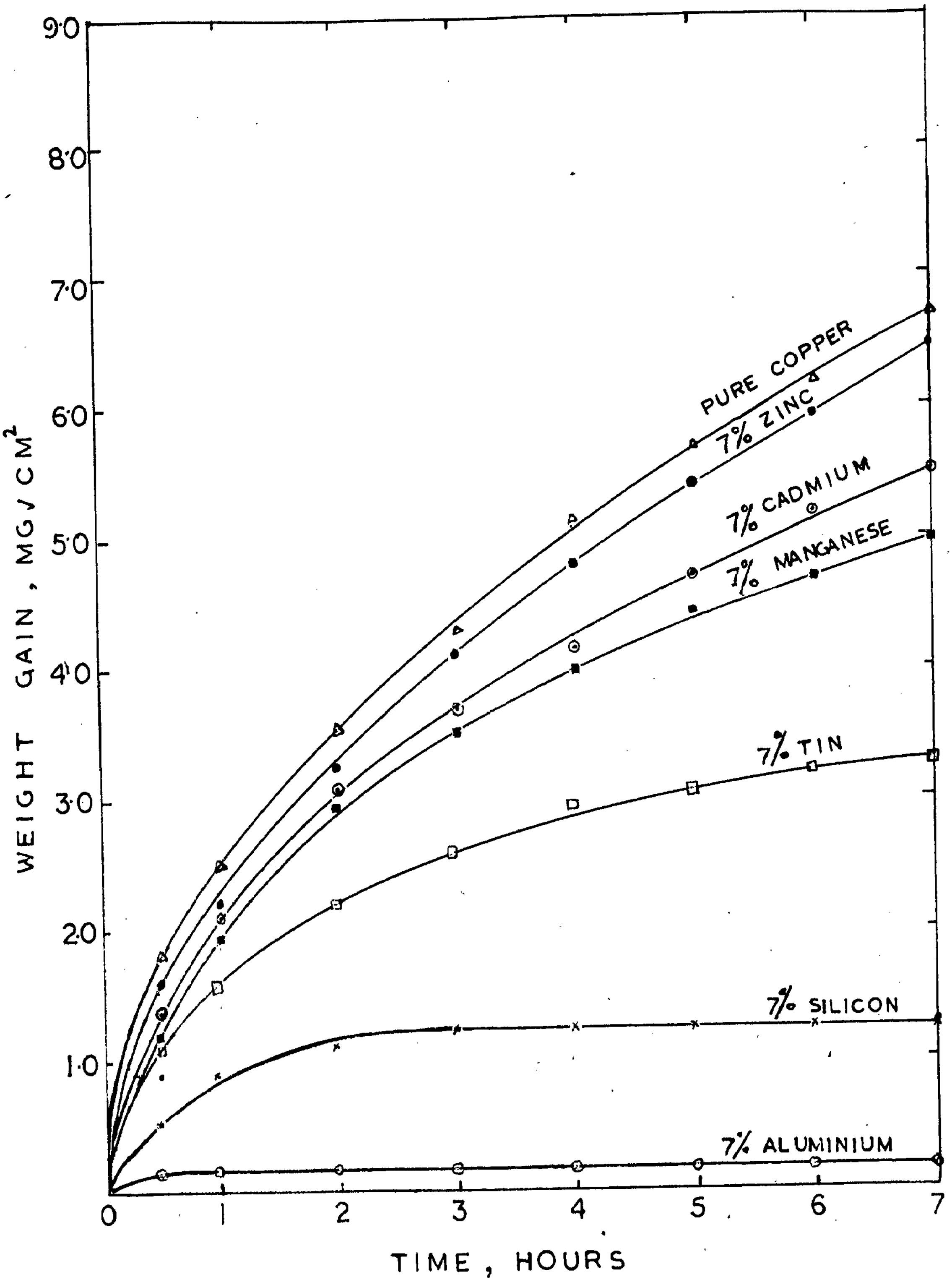


FIG 54. EFFECT OF VARIOUS ALLOYING ELEMENTS ON THE OXIDATION KINETICS OF COPPER AT 700°C

III-2. DISCUSSION

From the results of pure Copper oxidation in air at various temperatures (figure 25), it is observed that the curves follow a parabolic path in the entire temperature range from 500 to 900°C. However, when the square of weight gain per unit area has been plotted against time (figure 39), the points fall very close to straight lines for all temperatures except at 500°C, where the points fall away from the straight line. During the initial period of oxidation they are above the line and below the line during the later stages. This suggests that the oxidation of Copper takes place according to the parabolic law in the temperature range 600 to 900°C, and around 500°C, either the logarithmic law or the cubic law may be expected. To confirm this, the weight gain per unit area at 500°C has been plotted against time on log scale. A straight line was obtained (figure 43), suggesting confirmity with a logarithmic law. The results are in good agreement with those of Tylecote[9].

The slope of the lines on the parabolic plot (figure 39) gives the parabolic rate constant (k_p), and when the logarithm of parabolic rate constant is plotted against the reciprocal of temperature in absolute, a straight line is obtained. The slope of this line is 0.513×10^4 and from this the activation energy has been calculated to be equal to 23.16 ± 3 K Cal/mole, which is in good agreement with the values of pilling and Bedworth[4].

Figure 26 to 30 shows the effect of Zinc additions on the oxidation kinetics of Copper. Upto 15% Zinc additions the oxidation was nearly same as in pure Copper (figures 26 & 27). But at higher concentrations of Zinc the oxidation resistance was found to increase tremendously (figure 28 to 30). This became more clear when the weight gain due to oxidation in 7 hours has been plotted against the percentage of Zinc in the alloy (figure 52). This may be attributed to the fact that in alloys having less than 15% Zinc, the scale consists of a Cu_2O matrix with ZnO particles embedded, whereas in alloys having more than 15% Zinc, a continuous ZnO film is formed which is highly protective, as suggested by Dunn[8].

Figure 40 shows the parabolic plot for the oxidation of Copper-Zinc alloys at 700°C. Plot shows straight line for Cu-7% Zinc and Cu-15% Zn alloys, confirming that the oxidation of these two alloys is governed by the parabolic law. However, in case of Cu-30% Zn and Cu-40% Zn alloys, the curves shows straight line upto about oxidation time of one hour and then the oxidation behaviour is found to deviate from the parabolic behaviour. From the straight line portions of the curves the values of rate constants have been calculated to be $k_p = 2.1 \times 10^{-2}$ mg^2/Cm^4 min. for Cu-20% Zn alloy and $k_p = 0.6 \times 10^{-2} mg^2/Cm^4$ min. for Cu-30% Zn alloy.

The deviation from the straight lines in figure 40 suggests that a logarithmic law may be valid. To check this the weight gain per unit area has been plotted against time on log scale (figure 44). A straight line is obtained which confirms the oxidation follows a logarithmic law.

Figures 31 to 33 shows the weight gain vs time plots for oxidation of Copper -Aluminium alloys. It is clear from figure 33, that 7% aluminium gives very good resistance to oxidation. In case of Copper-2% Aluminium, it is observed that oxidation is less at 800°C as compared to 700 and 900°C (figure 31). This becomes more clear when the weight gain in 7 hours oxidation has been plotted against temperature (figure 53). A minima is observed at 800°C. It may be due to the formation of a more adhering and continuous oxide layer at this temperature as proposed by Dennison and Preece[5].

It seems that oxidation proceeds rapidly until a protective film of alumina is formed at the oxide/metal interface and then oxidation practically ceases. It is observed that the oxidation of Copper-Aluminium alloys does not follow the usual parabolic law. The plot of weight gain per unit area vs log of time gives a straight line which shows that the logarithmic law is obeyed (figures 45 to 47) in the range under consideration.

Figures 35 and 36 shows the effect of 3% and 7% Silicon in Copper respectively. It is observed that both the alloys are good oxidation resistant only upto 700°C and beyond which the oxidation resistance decreases. This may be attributed to the fact that at temperatures upto 700°C, a thin film of Silica is formed at the scale/metal interfaces which gives resistance to oxidation, but at higher temperatures the film of Silica was not evident[5]. From the plots shown in figure 48 and 49 it is clear that oxidation upto 700°C takes place according to the logarithmic law and above this temperature the usual parabolic law is observed (figure 35 & 36).

Figure 34 shows the weight gain vs time plot for the oxidation of Copper-7% Tin alloy at temperatures from 500 to 900°C, from which it is clear that tin increases the oxidation resistance of Copper to some extent. The weight gain per unit area vs log time plot shows straight lines for all temperatures (figure 50). This confirms that the oxidation is governed by logarithmic law in this temperature range.

Figure 37 and 38 shows the effect of 7% Manganeses and 7% Cadmium respectively on the oxidation kinetics of Copper. It is observed that the oxidation is nearly the same as in case of Copper, and the oxidation follows a parabolic law (figure 41 & 42).

Figure 54 gives the comparative idea of the effect of small additions(7 wt%) of Aluminium, Silicon, Tin, Manganese, Cadmium and Zinc individualy on the oxidation kinetics of Copper. The effectiveness of these additions in conferring resistance to oxidation is found to decrease in the above order. This can be correlated to the electrical conductivity of the oxides of the additives. Price and Thomas[25] have calculated the electrical conductivities of various oxides at 1000°C. From the values given by them it is observed that the electrical conductivity of the oxides of the additives under consideration increases in the following order;Aluminium, Silicon ,Tin etc. From this it can be concluded that the metals ~~oxides~~ which have oxides of low electrical conductivity will contribute higher oxidation resistance to Copper.

CONCLUSIONS

From the oxidation study of pure Copper in air in the temperature range 500 to 900 °C, it can be concluded that the oxidation is governed by the parabilic law in the temperature range 600 to 900 °C, while at 500°C, logarithmic law is valid. The parabolic rate constants vary with temperature in the normal way, i.e. a plot of log k against 1/T is a straight line.

From the oxidation studies of various Copper-base alloys in the temperature range 500 to 900 °C, it can be concluded that those elements which have oxides of low electrical conductivity, e.g. Aluminium and Silicon, impart higher resistance to oxidation, except for higher amounts of Zinc, which gives high resistance to oxidation inspite of having higher electrical conductivity. This can be attributed to the fact that the Zinc oxide is a excess-cation type semiconductor.

It can be concluded that the ability of an alloying element to reduce the oxidation rate depends on the formation of a separate and continuous layer of its oxide at the scale/metal interface which prevents outward diffusion of Cu^+ ions by virtue of a high electrical resistivity.

SUGGESTIONS FOR FURTHER WORK

It is suggested that following investigations may be carried out to obtain a better understanding of the effects of various variables on the oxidation kinetics of Copper.

(i) Experiments must be conducted in oxygen atmosphere and the effect of gas pressure and concentration on the oxidation kinetics of Copper and its alloys, should be studied.

(ii) Various additives must be added in wide ranges of concentration in Copper and their effect on oxidation kinetics of Copper should be studied in greater detail.

(iii) Efforts must be made to find out the critical concentration of additives in Copper after which the rate of oxidation is not much or is adversely affected.

(iv) Attempt should be made to study the effect of change in shape(helical, strip etc.) and size of the specimen on their oxidation.

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APPENDIX

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TABLE - I : OXIDATION DATA FOR PURE COPPER

TIME (in hours)	WEIGHT GAIN (in mg/Cm^2) AT				
	500°	600°	700°C	800°C	900°C
0.5	0.71	1.0	1.73	2.45	2.64
1	0.92	1.54	2.64	3.46	3.80
2	1.1	1.87	3.74	5.05	5.43
3	1.28	2.12	4.50	6.20	6.74
4	1.35	2.55	5.32	7.30	7.72
5	1.43	2.86	5.96	8.03	8.57
6	1.50	3.08	6.34	8.83	9.45
7	1.55	3.18	6.92	9.54	10.20

TABLE-II: OXIDATION DATA FOR COPPER-ZINC ALLOYS

TABLE - II (a)

TIME (in hours)	WEIGHT GAIN FOR (mg/Cm^2)								
	Cu-7% Zn Alloy AT			Cu-15% Zn Alloy AT			Cu-20% Zn Alloy AT		
	500°C	600°C	700°C	500°C	600°C	700°C	500°C	600°C	700°C
5	0.61	0.89	16.4	0.54	0.81	1.57	0.50	0.82	1.10
1	0.85	1.32	2.23	0.78	1.18	2.09	0.71	1.10	1.35
2	1.14	1.75	3.24	1.01	1.34	2.91	0.80	1.30	1.71
3	1.29	2.01	4.09	1.18	1.72	3.64	0.82	1.57	1.85
4	1.34	2.35	4.78	1.25	1.98	4.19	0.85	1.62	1.92
5	1.39	2.50	5.41	1.28	2.29	4.93	0.87	1.75	2.01
6	1.41	2.75	5.92	1.32	2.53	5.32	0.90	1.82	2.30
7	1.42	2.85	6.47	1.34	2.57	6.24	0.92	1.82	2.32

TABLE - II (b)

TIME (hours)	WEIGHT GAIN (in mg/Cm^2) FOR					
	Cu-30% Zn Alloy AT			Cu-40% Zn Alloy AT		
	500°C	700°C	900°C	500°C	700°C	900°C
0.5	.31	.43	.52	.20	.28	.35
1	.40	.60	.61	.31	.35	.44
2	.52	.78	.95	.37	.42	.52
3	.53	.85	1.01	.40	.47	.57
4	.54	.92	1.10	.41	.50	.60
5	.55	.97	1.13	.41	.52	.62
6	.55	.99	1.15	.41	.54	.62
7	.55	.99	1.15	.41	.56	.62

TABLE-III: OXIDATION DATA FOR COPPER-ALUMINIUM ALLOYS

TIME (in Hours)	WEIGHT GAIN (in mg/Cm^2) FOR									
	Cu-2% Al Alloy AT				Cu-4% Al Alloy AT				Cu-7% Al Alloy AT	
	600°C	700°C	800°C	900°C	600°C	700°C	800°C	900°C	700°C	900°C
.5	.51	1.21	0.85	1.41	.25	.62	.57	0.82	.05	.16
1	.92	1.56	1.20	1.92	0.51	1.01	.85	1.06	.09	.22
2	1.15	2.21	1.65	2.60	0.62	1.20	1.01	1.35	.11	.29
3	1.45	2.50	2.01	3.23	0.67	1.31	1.15	1.39	.12	.33
4	1.55	2.65	2.10	3.61	0.70	1.37	1.20	1.44	.14	.35
5	1.58	2.71	2.20	3.95	0.72	1.40	1.25	1.47	.15	.35
6	1.60	2.75	2.24	4.25	0.72	1.40	1.25	1.48	.15	.35
7										

TABLE -IV: OXIDATION DATA FOR COPPER-SILICON ALLOYS

TIME (in hours)	WEIGHT GAIN (in mg/Cm^2) FOR								
	Cu-3% Si Alloy AT					Cu-7% Si Alloy AT			
	500°C	600°C	700°C	800°C	900°C	600°C	700°C	800°C	900°C
.5	.35	.59	0.81	1.25	2.45	.26	.48	.78	1.55
1	.61	.91	1.14	2.02	3.44	.45	.76	1.28	2.19
2	.89	1.15	1.54	2.59	4.65	.63	.98	2.17	3.18
3	.94	1.31	1.79	3.09	5.39	.75	1.24	2.71	4.08
4	1.01	1.39	1.94	3.82	6.12	.82	1.26	3.14	4.67
5	1.02	1.48	2.01	4.42	6.71	.85	1.30	3.92	5.52
6	1.02	1.53	2.22	5.04	7.38	.87	1.30	4.48	5.76
7	1.02	1.55	2.25	5.43	7.81	.91	-	4.92	6.25

TABLE - V: OXIDATION DATA FOR COPPER-7% TIN ALLOY

TIME (in hours)	WEIGHT GAIN (in mg/Cm^2) AT				
	500°C	600°C	700°C	800°C	900°C
0.5	0.41	0.75	1.10	1.21	1.25
1	0.62	1.10	1.61	1.75	1.98
2	0.81	1.55	2.21	2.52	2.72
3	0.95	1.75	2.55	3.02	3.38
4	1.01	2.01	2.94	3.26	3.71
5	1.05	2.21	3.04	3.51	3.98
6	1.12	2.32	3.21	3.71	4.08
7	1.15	2.39	3.25	3.85	4.25

TABLE - VI: OXIDATION DATA FOR COPPER-7% MANGANESE ALLOY

TIME	WEIGHT GAIN (in mg/Cm^2) AT				
	500°C	600°C	700°C	800°C	900°C
0.5	0.42	0.80	1.31	1.42	1.75
1	0.61	1.21	1.89	2.04	2.49
2	0.85	1.62	2.81	3.09	3.62
3	0.97	1.83	3.48	3.72	4.48
4	1.02	1.89	3.80	4.41	5.38
5	1.08	2.14	4.31	5.08	6.18
6	1.12	2.23	4.65	5.58	6.93
7	1.24	2.47	5.04	6.20	7.54

TABLE - VII: OXIDATION DATA FOR COPPER 7% CADMIUM ALLOY

TIME (in hours)	WEIGHT GAIN (in mg/Cm^2) AT				
	500°C	600°C	700°C	800°C	900°C
.5	0.45	0.76	1.39	1.81	1.98
1	0.72	1.17	2.18	2.65	3.15
2	0.89	1.52	3.01	3.74	4.51
3	1.01	1.92	3.71	4.70	5.12
4	1.09	2.12	4.30	5.43	6.24
5	1.24	2.30	4.68	6.01	7.05
6	1.38	2.47	5.14	6.69	7.60
7	1.45	2.71	5.48	7.22	8.32