

Effects of Temperature on the Oxidation Kinetics of Copper Alloys.

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ABSTRACT

When metals are placed in a high temperature environment, oxidation of such metals occurs when the oxide film or scales begins to form on their surfaces. The mechanism of oxidation depends on the nature of the scales that are formed, which could be solid, liquid, or gas. The effect of temperature on the oxidation kinetics of copper and some alloys were studied and it was observed that temperature has a significant effect on the properties of copper and some of its alloys through change in the oxidation kinetics.

(Keywords: temperature, oxidation kinetics, copper, alloys, oxide films)

INTRODUCTION

When metals are placed in a high temperature environment, oxidation of such metals occurs when oxide film or scale begins to form on their surfaces. The mechanism of oxidation depends on the nature of the scales that is, whether the oxide is solid, liquid, or gaseous. When solid scales are formed, the oxidation behavior depends on whether the scales are compact or porous.

A compact scale acts as a barrier, which separates the metal and the oxygen gas. If sufficient oxygen is available at the oxide surface, the rate of oxidation at high temperature will be limited by a solid diffusion, for example lattice grain boundary or short circuit diffusion through the compact scale. As the diffusion distance increases and as the oxide grows in thickness, the rate of reaction will decrease with time (Davies, D.E.).

Wagner's theory, as it applies to compact scales of reaction products; it is assumed that a volume-

diffusion of the reacting ions (or corresponding point defects) or a transport of electrons across the growing scale is the rate-determining process of the total reaction.

Electrons and ions are considered to migrate independently of each other. As diffusion through the scale is rate determining, reactions at phase boundaries are considered rapid, and it is assumed that thermodynamic equilibrium is established between the oxide and the oxygen gas at the oxide/oxygen interface and between the metal and the oxide at the metal/oxide phase boundary.

The driving force of the reaction is the free-energy change associated with the formation of the oxide MO from the metal M and the oxygen gas, and as a result, concentration gradients of the components are established in the oxide.

EFFECT OF TEMPERATURE ON DIFFUSION

A concentration gradient within a homogenous solid phase causes diffusion of the atoms or ions via interstitial or vacant lattice sites. According to Fick's Law, the amount of solute in diffusing a certain cross-section. (A) per second is proportional to the concentration gradient dc/de at this plain:

$$M = -AD (dc/de) \quad (1)$$

where (D) is the diffusion coefficient, which is generally determined and tabulated. Then the rate of change of the concentration (C) at a point where the concentration gradients is dc/de .

$$dc/dt = d/de (D dc/de) \quad (2)$$

and if (D) is taken to be independent of concentration:

$$dc/dt = D d^2c/de^2 \quad (3)$$

when there are two species (A) and (B), with individual chemical diffusion coefficient D_A and D_B , then:

$$D = N_A D_A + N_B D_B \quad (4)$$

where (N_A) and (N_B) donate the mole fractions. That zinc and copper atoms move at different rate for a brass of given concentration at a given temperature.

The temperature dependence of reaction rates is governed by an exponential relations known as the Arrhenius equation, corresponding to this equation, the temperature dependence of diffusion rates is generally written in the form:

$$D = D_0 e^{-Q/RT} \quad (5)$$

where (D_0) and (Q) are constants. Both these equations are particular forms of the Boltzmann relationship between the temperature and the percentage of molecules in a gas having energies exceeding a certain threshold value.

Since the diffusion rates may depend on concentration, the Arrhenius equation should only be applied at constant concentration. However,

when the logarithms of chemical inter-diffusion coefficients are plotted against $1/T$, they may occasionally be found to be represented by two intersecting straight lines according to:

$$D = D_{0a} (e^{-Q_1/rt}) + D_{0b} (e^{-Q_2/rt}) \quad (6)$$

Indicating that two different mechanisms determine the rates of low and high temperature. In ionic crystals this may be due to the diffusion of one specie having a different activation energy from that of the other, while the diffusion rates of both specie are of approximately the same order. An example of the above equation is seen in the reaction of copper with oxygen which is plotted against the inverse of temperature there is a distinct break in the curve corresponding to a two-term expression.

$$K = A_1 e^{-Q_1/rt} + A_2 e^{-Q_2/rt} \quad (7)$$

Although, in this illustration, the actual Arrhenius equation is used i.e.:

$$K = A e^{-Q_1/RT} \quad (8)$$

where K = rate constant,
 A is a constant,
 Q = Activation energy.

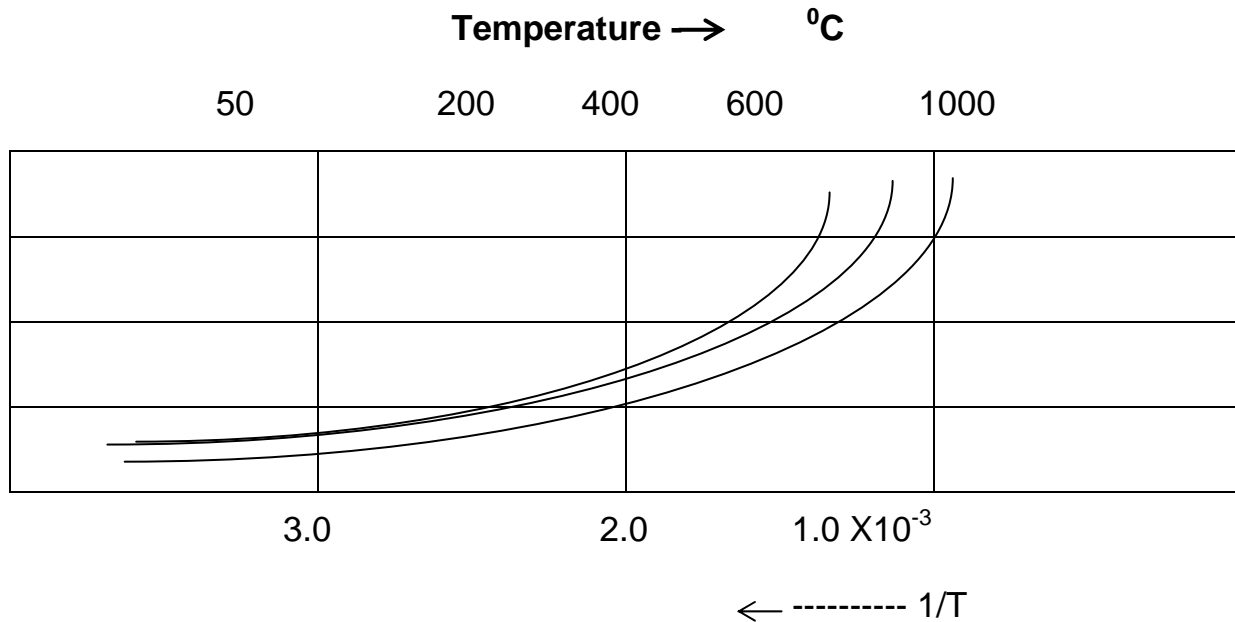


Figure 1: Dependence of Oxidation rate of Copper on Temperature (Kabashevsk and Hopkins).

The activation energy calculated from the high and low temperature straight lines are 157,736,8 and 84,265.76 joules, respectively. Under the conditions of high temperature reaction CuO is not stable and Cu₂O is the oxide present, at low temperature, another reaction that is rate determining appears to be CuO. The equation of the type 3.3-6 may also be due to grain boundary diffusion being rate determining at a low temperatures and trans-granular diffusion at high temperature.

With alloys, the transition temperature is relatively low, but with oxides, which often have melting points higher than the metals, the grain boundary may predominate even at relatively high temperature.

OXIDATION – TIME RELATIONSHIPS

The type of time relationship that can be applied to a given metal or alloy depends largely on the thickness of the film already formed, that is in time and temperature. Since the transition from one time relationships to another are smooth and depend on thickness, the tables below give only a rough outline of the actual observations.

It is observed in oxidation films that at low temperature, logarithmic and inverse logarithmic relationships prevail, literature has shown that many metals when exposed to oxygen at the oxidation rate drops to low or negligible value, a stable minutes thickness 20-50A⁰ being formed.

EXPERIMENTAL PREPARATION OF CU-ALLOY STRIPS

Five different types of copper alloys were prepared for investigation. They are listed as follows:

(i)	95% Cu	-	5% Zn
(ii)	85% Cu	-	15% Zn
(iii)	70% Cu	-	30% Zn
(iv)	95% Cu	-	5% Sn
(v)	90% Cu	-	10% Sn

Each alloy was cast by first cutting a copper ingot into five different pieces after which each piece was weighed. Small pieces of Tin (Sn) and Zinc (Zn) were cut off ingots.

To form 97% Cu – 5% Zn for instance, the mass of Zn that could be evaporated because the melting of Cu is very much higher than that of Zn and Sn. This process was repeated for all alloys.

Having done this, sand moulds were prepared using a wooden pattern which had dimension of 4MM thickness, 4cm breadth, and 10cm long. The sand consisted of silica with about 10% of clay as a binding agent. Each of the mould was made in two part in order to facilitate removal of the pattern and the spure pin feeder of the cast alloy had the same dimensions as that of the wooden pattern used in preparing sand mould.

The alloys were prepared by putting each copper ingot in a graphite crucible which was then placed inside a furnace and heated to 1200⁰C. at about this temperature, Cu was already in the liquid form. The alloying metal was added to the molten copper and the liquid metal stirred continuously for homogenous mixing. When the alloy had been heated for four minutes, it was then poured into the sand moulds.

After the cast alloy had solidified and cooled to room temperature, it was rolled to reduce its thickness from 4mm to 1mm representing a 75% reduction by cold work. This procedure was repeated for the rest of the alloys.

RESULTS AND ANALYSIS

1. Temperature of operation = 800⁰C
2. Length of specimens = 5.0cm
3. Breadth of specimen = 1.0cm
4. Surface area of specimen = 2(1x5) = 10cm²
5. Initial thickness = 4cm
6. Final thickness = 1mm
7. Percentage reduction = 75%

Symbols

T	=	Time
M	=	Mass of Crucible
M + m	=	Mass of crucible and specimen before oxidation
M + m*	=	Mass of crucible and specimen after oxidation

Table 1: Mass values and mass increment values with time before and after oxidation for Specimen A: 100% Cu at 800°C.

Time, t (min)	M (gm)	(M + m) (gm)	(M + m*) (gm)	ΔM (gm)
10	14.3988	19.6021	19.6515	0.0494
30	14.5069	19.6008	19.6955	0.0947
60	14.5180	19.8915	20.0242	0.1327
90	14.2155	20.6908	20.8518	0.1610
120	14.7467	20.3808	20.5678	0.1870

Calculation of Film Thickness (X):

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \rho \quad (9)$$

$$\text{Change in Volume} = \frac{\Delta m}{\rho} = v \quad (10)$$

$$2(5.0 \times 1.0 \times X) = \frac{\Delta m}{\rho} = \frac{\Delta m}{6} \quad \rho = 6 \text{ for pure copper}$$

$$X = \frac{\Delta m}{6 \times 2 \times 5.0} = \frac{\Delta m}{60} \quad (11)$$

Table 2 : Mass values, mass increment value/area with time before and after oxidation for Specimen B: 95% Cu – 5% Sn at 800°C.

Time, t (min)	M (gm)	(M + m*) (gm)	M (gm)	W(gmcm ⁻²)	W ² (gmcm ⁻²) ²
10	14.6136	19.6818	0.0374	3.74 x 10 ⁻³	1.4 x 10 ⁻⁵
30	14.6972	20.3217	0.0701	7.01 x 10 ⁻³	4.9 x 10 ⁻⁵
60	14.5241	20.3875	0.1062	10.62 x 10 ⁻³	11.28 x 10 ⁻⁵
90	14.6459	21.0255	0.1358	13.58 x 10 ⁻³	18.44 x 10 ⁻⁵
120	14.7155	21.6380	0.1541	15.41 x 10 ⁻³	23.84 x 10 ⁻⁵

Table 3 : Mass values, mass increment values/area with time before and after oxidation for Specimen C: 90% Cu – 10%Sn at 800°C.

Time, t (min)	M (gm)	(M + m) (gm)	(M + m*) (gm)	Δm (gm)	W (gmcm ⁻²)	W ² (gmcm ⁻²) ²
10	14.4202	19.4946	19.5156	0.0210	2.1 x 10 ⁻³	4.41 x 10 ⁻⁶
30	14.7224	19.8272	19.8812	0.0540	5.4 x 10 ⁻³	29.16 x 10 ⁻⁶
60	14.7210	19.9686	20.0503	0.0817	8.17 x 10 ⁻³	66.75 x 10 ⁻⁶
90	14.9092	20.2043	20.3258	0.1115	11.15 x 10 ⁻³	124.3 x 10 ⁻⁶
120	14.7528	20.2996	20.4170	0.1174	11.74 x 10 ⁻³	137.8 x 10 ⁻⁶

Table 4 : Mass values, mass increment values/area with time before and after oxidation for Specimen D: 95% Cu – 5%Sn at 800^oC.

Time, t (min)	M (gm)	(M + m*) (gm)	(M + m*) (gm)	W(gmcm ⁻²)	W(gmcm ⁻²) ²
10	14.4450	19.8985	19.9137	0.0152	1.52 x 10 ⁻³
30	14.5970	19.8130	19.8513	0.0383	3.83 x 10 ⁻³
60	14.5180	19.8915	20.0242	0.1327	8.17 x 10 ⁻³
90	14.7204	20.5784	20.6807	0.1023	10.23 x 10 ⁻³
120	14.5503	20.2120	20.3504	0.1420	14.20 x 10 ⁻³

Table 5: Mass values, mass increment values/area with time before and after oxidation for Specimen E: 85% Cu – 15%Zn at 800^oC.

Time, t (min)	M (gm)	(M + m) (gm)	(M + m*) (gm)	Δm (gm)	W(gmcm ⁻²)
10	14.7642	19.3000	19.3101	0.0101	1.01 x 10 ⁻³
30	14.7279	19.6700	19.6968	0.0268	2.68 x 10 ⁻³
60	14.7140	19.7185	19.7824	0.0630	6.39 x 10 ⁻³
90	14.6151	20.7751	19.8600	0.0949	9.4 x 10 ⁻³
120	14.5177	21.1175	21.3334	0.1191	11.91 X 10 ⁻³

Table 6: Mass values, mass increment values/area with time before and after oxidation for Specimen F: 85% Cu – 15%Zn at 800^oC.

Time, t (min)	M (gm)	(M + m) (gm)	(M + m*) (gm)	Δm (gm)	W(gmcm ⁻²)
10	14.6452	19.4302	19.4353	0.0051	5.1 x 10 ⁻⁴
30	14.8062	19.9471	19.9574	0.0203	20.3 x 10 ⁻⁴
60	14.8600	19.0221	19.0710	0.0480	48.0 x 10 ⁻³
90	14.6742	19.9442	19.0017	0.0675	67.5 x 10 ⁻⁴
120	14.6094	20.4640	21.5560	0.0920	92.0 x 10 ⁻⁴

Temperature of Operation; -200^oC

Length of specimen	=	5.0cm (Cu above)
Breadth of specimen	=	3.0cm
Surface of area of specimen	=	2 x 15.0cm ² = 30cm ²
Length of Alloys Specimen	=	4.5cm
Initial Thickness	=	4mm
Final thickness	=	1mm
Percentage reduction	=	75%

Symbols

T	=	Time
M	=	Mass specimen before oxidation
M*	=	Mass specimen after oxidation
ΔM	=	Increase in weight = (M – m*)
W	=	ΔM / (Area of specimen)

Table 7 : Mass values, mass increment values/area with time before and after oxidation for Specimen G: 100% Cu at 200°C.

Time, t (min)	M (gm)	(M + m) (gm)	(M + m) (gm)	Δm (gm)	W(gmcm ⁻²)
1.0	14.3818	14.3832	0.0005	1.55 x 10 ⁻⁵	2.40 x 10 ⁻⁴
2.0	14.7266	14.7275	0.0007	2.37 x 10 ⁻⁵	5.62 x 10 ⁻⁴
3.0	14.7414	14.7423	0.0009	2.96 x 10 ⁻⁵	8.76 x 10 ⁻⁴
4.0	14.3006	15.3016	0.0010	3.34 x 10 ⁻⁵	11.15 x 10 ⁻⁴

Calculation of Film Thickness (x)

$$\rho = \frac{\Delta m}{\Delta v} \quad (12)$$

$$\text{Change in Volume} = \Delta v = \frac{\Delta m}{\rho} = \frac{\Delta m}{6}$$

Since ρ = 6 for pure copper

$$\Delta v = 2(5 \times 3 \times X) = \frac{\Delta M}{6}$$

$$X = \frac{\Delta m}{5 \times 3 \times 2 \times 6} = \frac{\Delta m}{180}$$

Table 8: Film thickness (x) with time for Cu at 200°C.

Time, t (min)	x (cm)	x ² (cm ²)
1.0	2.78 x 10 ⁻⁶	7.72 x 10 ⁻¹²
2.0	3.87 x 10 ⁻⁶	1.512 x 10 ⁻¹¹
3.0	5.0 x 10 ⁻⁶	2.50 x 10 ⁻¹¹
4.0	5.56 x 10 ⁻⁶	3.09 x 10 ⁻¹¹

Table 9: Mass values, mass increment values/area with time before and after oxidation for Specimen H: 95% Cu – 5%Zn at 200°C.

Time, t (min)	M (gm)	M* (gm)	Δm (gm)	Δm (gm ⁻²)	W ² (gmcm ⁻²) ²
1.0	13.8995	13.8998	0.0003	1.1 x 10 ⁻⁵	1.23 x 10 ⁻¹⁰
2.0	12.3360	12.3364	0.0004	1.4 x 10 ⁻⁵	2.19 x 10 ⁻⁶
3.0	14.4835	14.4840	0.0005	1.85 x 10 ⁻⁵	3.43 x 10 ⁻⁶
4.0	14.8789	14.8795	0.0006	2.22 x 10 ⁻⁵	4.94 x 10 ⁻⁶

Temperature of Operation: -100°C

- Length of Copper Specimen = 5.0cm
 - Length Alloys Specimen = 4.5cm
 - Breadth of Specimen = 3.0cm
 - Length of Copper Specimen = 2 x (5 x 3) = 30cm²
 - Surface Area of Alloy Specimen = 2 x (4.5 x 3) = 27cm²
 - Initial Thickness = 4mm
 - Final Thickness = 1mm
 - Percentage Reduction = 75%
- Symbols are the same as those of 200°C

Table 10: Mass, mass increment, mass increment/area and time relationships for Specimen I:
100% Cu at 100°C.

Time, t (min)	M (gm)	M* (gm)	Δm (gm)
1.0	14.7559	14.7572	0.0013
2.0	14.1953	14.1967	0.0014
3.0	14.5484	14.5499	0.0015
4.0	14.2604	14.2626	0.0016

Time, t (sec)	W (gcm ⁻²)	W ² (gcm ⁻²) ²	Log (t+1)
72.00	4.35 x 10 ⁻⁹	1.89 x 10 ⁻⁹	8.882
144.00	4.65 x 10 ⁻⁹	2.16 x 10 ⁻⁹	9.575
216.00	5.00 x 10 ⁻⁹	2.50 x 10 ⁻⁹	9.980
288.00	5.35 x 10 ⁻⁹	2.86 x 10 ⁻⁹	10.268

Table 11: Mass, mass increment, mass increment/area and time relationships Specimen J:
95% Cu – 5% Zn at 100°C.

Time, t (hrs)	M (gm)	M* (gm)	Δm (gm)
2.0	13.9419	13.94267	0.0008
4.0	12.9404	14.4413	0.0009
6.0	12.2937	12.2947	0.0010
8.0	12.1943	12.1954	0.0011

Time, t (sec)	W (gcm ⁻²)	W ² (gcm ⁻²) ²	Log (t+1)
72.00	2.96 x 10 ⁻⁵	8.76 x 10 ⁻¹⁰	8.882
144.00	3.35 x 10 ⁻⁵	11.22 x 10 ⁻¹⁰	9.575
216.00	3.75 x 10 ⁻⁵	14.06 x 10 ⁻¹⁰	9.980
288.00	4.08 x 10 ⁻⁵	16.6 x 10 ⁻¹⁰	10.268

Table 12: Mass, mass increment, mass increment/area and time relationships for Specimen K:
95% Cu – 5%Sn at 100°C.

Time, (hr)	W (gm)	M(gm)	Δm(gm)
2.0	14.7465	14.7471	0.0005
4.0	13.7235	13.7242	0.0006
6.0	12.5747	12.5754	0.0007
8.0	12.0488	12.0496	0.0008

Time, (se)	W (gcm ⁻²)	W ² (gcm ⁻²) ²	Log (t+1)
72.00	2.22 x 10 ⁻⁵	4.93 x 10 ⁻¹⁰	8.882
144.00	2.59 x 10 ⁻⁵	6.71 x 10 ⁻¹⁰	9.575
216.00	2.59 x 10 ⁻⁵	6.71 x 10 ⁻¹⁰	9.980
288.00	2.96 x 10 ⁻⁵	8.76 x 10 ⁻¹⁰	10.268

DISCUSSION AND OBSERVATIONS

It is observed that oxidation of pure copper obeys a parabolic rate at 200°C and 800°C. The oxidation rate of the metal however obeys logarithmic rate law at 100°C. Alloy the containing 95%Cu–5%Sn obeys parabolic rate law at 200°C and 800°C. This is because at these two temperatures, the ionic diffusion flux is inversely proportional to the thickness of diffusion barrier. This occurs when the ions present in the alloy move outwards through the film. This is true for an alloy containing 90%Cu – 10%Sn 800°C, for specimen C.

At 100oC, the oxidation rate of alloy containing 95%Cu – 5%Zn, 95%Cu – 5%Sn obey Logarithm rate law. As the oxide film formed thickness, it acts as barrier to the outward movement of ions making films growth impossible thereby obeying logarithmic rate law.

Values for specimen D & E shows that all the alloy of Cu and Zn that is 95%Cu – 5%Cu – 5%Zn, 85%Cu – 15%Sn obeys liner, rate law at 800°C. This is an indication that there were porous or cracked scales present in all the alloys so the scale did not represent a diffusion barrier.

CONCLUSION

Oxidation of copper obeys parabolic rate law from 200°C upwards and follows the logarithmic rate law at lower temperature of about 100°C. Addition of tin and zinc to copper to form alloys (bronzes and brasses) increase the oxidation resistance of copper.

The greater the percentage of the metals, the greater the resistance of the alloys to oxidation. Tin gives copper a better resistance to oxidation than zinc when both are investigated at the same composition by weight and at the same temperature.

Tin also gives better oxidation resistance when alloyed with copper than zinc at high temperature. This is because alloy of copper and zinc obey linear rate law at high temperature and this implies that there are cracks or cavities that run at angle to its surface.

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