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The High Temperature Oxidation of AlSil2CuNi Aluminium Alloy

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ABSTRACT

For the oxidation process, the alloy samples in rod form are oxidized in the oxygen atmosphere for the time intervals of 2, 4, 6, 8, 24 hours at temperatures 300, 400 and 500°C. The oxidation phenomena for this alloy has been investigated by the measurements of the increase in mass of the samples after the oxidation period. By the helps of the graphs of the functions increasing in mass in unit area (W) versus time (t), $W = f(t)$, at each temperature degree the kinetic equation for the oxidation of this alloy were oatained.

INTRODUCTION

In recent years, the all kinds of aluminium alloys are used widely in all branches of technological area.

In Turkey, the aluminium alloy AlSil2CuNi are produced in AL-TES Aluminium Plant in Seydişehir-KONYA. This alloy is coded in Turkish standard as Etial-145.

Etial-145 alloy is widely used for all kinds of motor piston production in car engines.

In this study, the high temperature oxidation at 300, 400 and 500°C in oxygen atmosphere has been investigated kinetically by the help of the determination the increase in mass of the specimens after the oxidation period.

THEORETICAL

The oxidation phenomena for a metal sample can be explained by the electron capture at the binaries of Metal/Oxide and Oxide/Gas.[3] This phenomena is shown in Fig. 1.-

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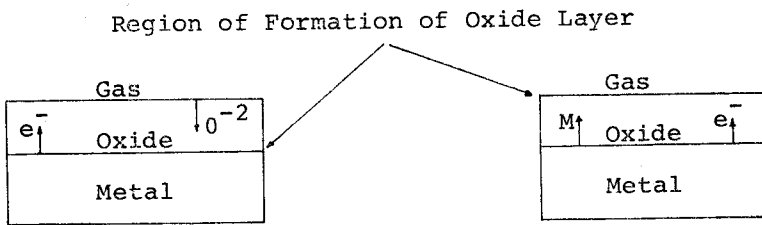
Region of Formation of Oxide Layer

Fig.1. Controled growth of dense layers of oxide, either by diffusion
of oxygen (left) or by diffusion of metal (right)

The reasons which cause the Oxidation of a metal sample can be summarized in three cases.[1]

1. Metal-Oxide Crystal Lattice Defects.

In oxidation process, the produced metal oxide layer on the metal surface is not in the stoichiometric structure. So in the crystal lattice structure of the metal oxide layer, there are some lattice defects such as vacancy of cations (p-type metal oxide) and vacancy of anions (n-type metal oxide).

2. Electrical Potential Gradient.

The oxygen atoms adsorbed on the metal surface at the begining of the oxidation are formed a negative charged layer on the metal surface. So, an electrical potential gradient is produced between the metal surface and the metal itself. This electrical potential gradient is caused the moving of anions and cations vacancies in both directions.

3. Chemical Potential Gradient.

The difference in the material concentration between the inner and outher side of the metal oxide layer is caused the chemical potential gradient. The existence of the chemical potential gradient helps the moving of the anion and cation vacancies.

KINETIC VELOCITY EQUATIONS

The kinetic equations represent the formation of metal oxide layers in oxidation process can be expressed by the formulas as fallows.-

$$\triangle m = k_1 t \qquad \text{Linear Law} \tag{1}$$

$$(\triangle m)^2 = k_2 t \qquad \text{Parabolic Law} \tag{2}$$

$$(\triangle m)^3 = k_3 t \qquad \text{Cubic Law} \tag{3}$$

$$\triangle m = k_4 \log (at + 1) \text{ Logaritmic Law} \tag{4}$$

$$\frac{1}{\triangle m} = \frac{1}{\triangle m_0} - k_5 \log (at + 1) \text{ Inverse Logaritmic Law} \tag{5}$$

EXPERIMENTAL PROCEDURE

The experimental study for the high temperature oxidation of Etial-145 alloy has been made at 300, 400 and 500°C.

The rod form samples in 6 mm diameter are used. The surface of the samples are polished and made homogene by using the abrasives numbered as 600 and 800 No. After polishing, the samples are kept in n-hexan to protect them the effect of air.

A micro -balance in 1.0×10^{-5} g -cm^{-2} sensitivity is used for the determination the increase in mass ($\triangle m$) of the samples after oxidation.

Five rod form samples are used for each temperature and before the oxidation process, each sample was kept in the nitrogen atmosphere at the experimental temperature degree for 15 minutes.

After cooling the samples in a desiccator for 20 minutes the mass of each sample is determined. Than each sample is oxidized in a fixed flow-rate oxygen atmosphere (3 lt /min) at the experimental temperature degree for the time intervals 2, 4, 6, 8 and 24 hours.

RESULTS and DISCUSSION

The experimental results are shown in three tables. Table-1, 2, 3.

The graph of the function $W = f(t)$ which is obtained by using the experimental results of the Table-1. is seen in Figure. 2.

The equation $W^n = kt$ is used to obtain the growth law of the oxide layer on the metal surface.[1] This equation can be defined in logarithmic form as fallow.

Table 1: The experimental results for 500°C.

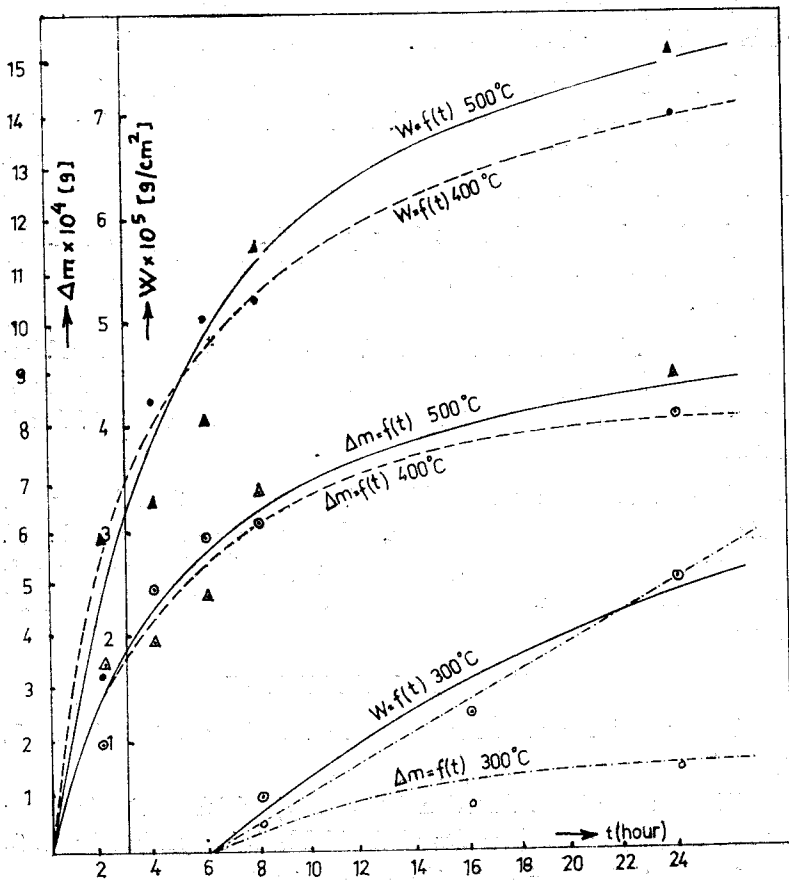| Sample No	Δm (g)	A (cm^2)	W(g.cm^{-2})	W^2(g^2.cm^{-4})	t(hours)
1	3.6×10^{-4}	11,87	3.03×10^{-5}	0.92×10^{-9}	2
2	4.0×10^{-4}	11,87	3.37×10^{-5}	1.14×10^{-9}	4
3	4.9×10^{-4}	11,97	4.13×10^{-5}	1.71×10^{-9}	6
4	6.9×10^{-4}	11,87	5.81×10^{-5}	3.38×10^{-9}	8
5	9.1×10^{-4}	11,87	7.67×10^{-5}	5.88×10^{-0}	24

Fig.2. Variation of the mass of oxide layer with time in linear scale

$$\log W^n = \log kt.$$

$$\log W = \frac{1}{n} \log t + \frac{1}{n} \log k \tag{6}$$

A logarithmic graph paper is used to obtain the graph of the function $W = f(t)$ at $500\,^{\circ}$C. The graph which is shown in Figure. 3. is a line. The value of (n) obtained by calculating the slope of this line is 2,01. This value shows us that the growth law of the oxide layer for $500\,^{\circ}$C is parabolic.

The graph of the function $W = f(t)$ which is obtained by using the experimental results of the Table-2. is seen in Figure. 2.

The obtained curve on the logaritmic graph paper is a line which consists of two parts as seen in Figure. 3. This shows us that the oxidation process takes place in two stages. The oxdation rate between the beginning of the oxidation and 4 hour is very rapid. The value of (n) for this time interval is obtned by calcu-lating the slope of the line ā and is found equals to 1. This value, $n = 1$, shows us that in the time period (0–4) hours at $400\,^{\circ}$C, the growth law of the oxide layer is linear and expressed by the equation of function $W = kt$.

The oxidation rate is decreased after 4 hour at $400\,^{\circ}$C. Another line, b̄, is obtained as seen in the Figure. 3 for the time interval (4–24) hours.

The obtained value of (n) for this time interval is found equals to 3. So this value shows us that the growth law of the oxide layer for the time interval (4–24) hours at $400\,^{\circ}$C is cubic and expressed by the equation of function $W^3 = kt$.

The graph of the function $W = f(t)$ which is obtained by using the experimental results of the Table-3. is seen in Figure. 2.

The obtained curve as seen in Figure. 2 can not be expressed by the equation $W^n = kt$. The curve is much close to a line expressed by an equation $y = mx-b$.

If the equation $W^n = kt$ is applied for $300\,^{\circ}$C, the obtained curve on the logaritmic paper is a line as seen in Figure 3. The value of (n) obtained by calculating the slope of this line is found equal to 0,7.

If the results shown on the Table-4 are examined, the function of temperature in the formation of oxide layer for this alloy is understood.
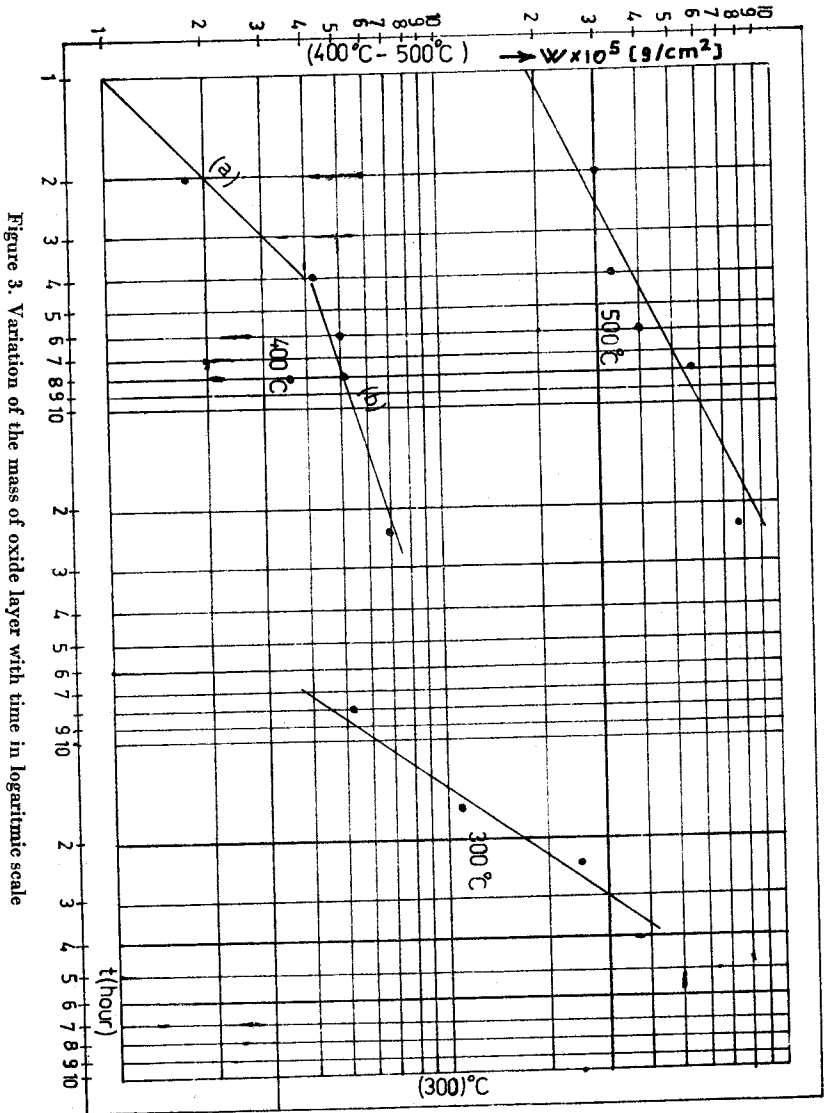

Figure 3. Variation of the mass of oxide layer with time in logaritmic scale

Table 2: The experimental results for 400°C

Sample No	Δm (g)	A(cm²)	W(g.cm⁻²)	W³(g³.cm⁻⁶)	t(hours)
1	2.0×10^{-4}	11.87	1.7×10^{-5}	0.5×10^{-14}	2
2	5.1×10^{-4}	11.87	$4./ \times 10^{-5}$	8.0×10^{-14}	4
3	6.0×10^{-4}	11.87	5.1×10^{-5}	13.0×10^{-14}	6
4	6.3×10^{-4}	11.87	5.3×10^{-5}	15.0×10^{-14}	8
5	8.3×10^{-4}	11.87	7.0×10^{-5}	34.0×10^{-14}	24

Table 3: The experimental results for 300°C

Sample No	Δm(g)	A(cm²)	W(g.cm⁻²)	t(hour)
1	—	—	—	2
2	—	—	—	4
3	—	—	—	6
4	$0,54 \times 10^{-4}$	9,26	$0,54 \times 10^{-5}$	8
5	$0,83 \times 10^{-4}$	6,41	$1,25 \times 10^{-5}$	16
6	$1,50 \times 10^{-4}$	5,77	$2,60 \times 10^{-5}$	24

As seen from the experimental results of the Table-4, for fixed time intervals as temperature increases the gain in mass takes place, so the thickness of the oxide layer increases. But theoretically this must cause a decrease in the oxidation rate[1,2]. We can say by looking the Figure 4, an oxide layer reached an enough thickness can stop the oxidation.

Table 4: The effect of temperature to the formation of oxide layer.

Temperature (°C)	W (g.cm⁻²)		
	2 hours	8 hours	24 hours
300	—	$0,54 \times 10^{-5}$	$2,60 \times 10^{-5}$
400	$1,70 \times 10^{-5}$	$5,30 \times 10^{-5}$	$7,00 \times 10^{-5}$
500	$3,03 \times 10^{-5}$	$5,81 \times 10^{-5}$	$7,67 \times 10^{-5}$

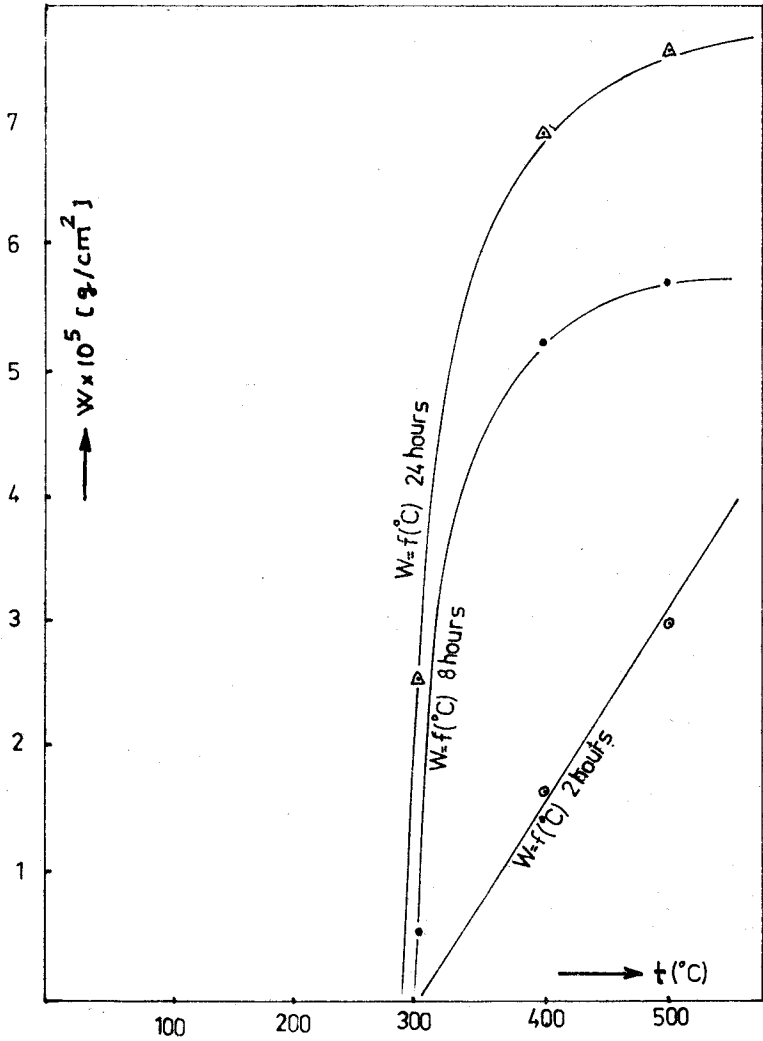Figure 4. Variation of the mass of oxide layer with temperature

CONCLUSION

In this study, the high temperature oxidation of AlSil2Cu-Ni alloy has been investigated. The experimental results shows that the effect of oxygen at the oxidation process is maximum at 500°C. But the thickness of the oxide layer increases rapidly

until 400°C. After 400°C, the increase in thickness and the mass of the oxide layer is slown down. This shows us that, after 400°C the formation rate of crystal lattice defects (cation and anion vacancies) in unit time in the oxide layer produced on the metal surface is decreased. This is a result of the oxidation theory.[2]

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ÖZET

Yapılan bu çalışmada, Etial-145 Alüminyum alaşımında 300°C, 400°C ve 500°C lerde alaşım üzerinde oluşan oksit-tabakasının sabit sıcaklıkta ve çeşitli zaman aralıklarında kütleleri saptanmıştır. Sabit sıcaklıkta birim yüzeyde oluşan oksit-tabaka kütlesinin zamana karşı grafikleri çizilmiş ve her sıcaklık derecesi için oksit-tabakasının büyüme kanunu saptanmıştır.

Ayrıca, sabit zaman aralığında alaşım üzerinde oluşan oksit-tabakasının kütlesinin sıcaklığa karşı grafikleri çizilmiş ve bu alaşımda sıcaklığın oksit-tabaka kütlesine etkisi araştırılmıştır.