General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

KINETICS AND MECHANISM OF THE OXIDATION PROCESS
OF TWO-COMPONENT Fe-Al ALLOYS

Hanna Przewlocka, Jolanta Siedlecka

STANDARD TITLE PAGE

1. Report No. NASA TM-77009	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle KINETICS AND MECHANISM OF THE OXIDATION PROCESS OF TWO COMPONENT Fe-Al ALLOYS		5. Report Date December 1982
		6. Performing Organization Code
7. Author(s) Hanna Przewlocka, Jolanta Siedlecka		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASw- 3542
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

This work presents results of studies of the oxidation process of two-component Fe-Al alloys containing I) up to 7.2% Al, and II) from 18 to 30% Al. Kinetic measurements were conducted using the isothermal gravimetric method in the range of temperature I) 1073-1223 K and II) 1073-1373 K respectively, for 50 hours. The methods used in studies of the mechanism of oxidation included: X-ray microanalysis, X-ray structural analysis, metallographic analysis and marker tests.

This work is a continuation of studies described in Reference [1], both papers giving a full picture of the process of oxidation of Fe-Al alloys containing up to 7.2% and 18-30% Al.

A mechanism for formation of scales on the investigated alloys is proposed on the basis of the obtained results.

17. Key Words (Selected by Author(s))	18. Distribution Statement
	Unclassified - Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 22	22. Price

KINETICS AND MECHANISM OF THE OXIDATION PROCESS OF TWO-COMPONENT Fe-Al ALLOYS

Hanna Przewlocka, Jolanta Siedlecka

I. INTRODUCTION

The problem of oxidation of two-component Fe-Al alloys has been an object of interest for the Department of General Chemistry of the Institute of Metallurgy at the Czestochowa Polytechnics. In this paper we present the results of studies on kinetics, morphological structure, and the chemical and phase composition of the product of oxidation. This work is a continuation of earlier studies on the kinetics and mechanism of the oxidation of two-component Fe-Al alloys. Results of the first part, which involved compositions with lower contents of aluminum, have been published already in Archiwum Hutnictwa [1]. This part extends the problem to higher ranges of temperatures and to higher contents of aluminum.

2. EXPERIMENTAL PART

Investigations were carried out on 7 types of two-component Fe-Al alloys, which were prepared from iron EO-4 (the contents of impurities did not exceed 0.16%) and aluminum class A-O 99.999% pure. The contents of the basic alloy component in particular alloys are given, among others, in Table 1. The process of melting the alloys, making the structure uniform and preparing samples for tests is described in [1]. Alloys were obtained with contents of aluminum up to 30% in which the contents of impurities did not exceed 0.18%.

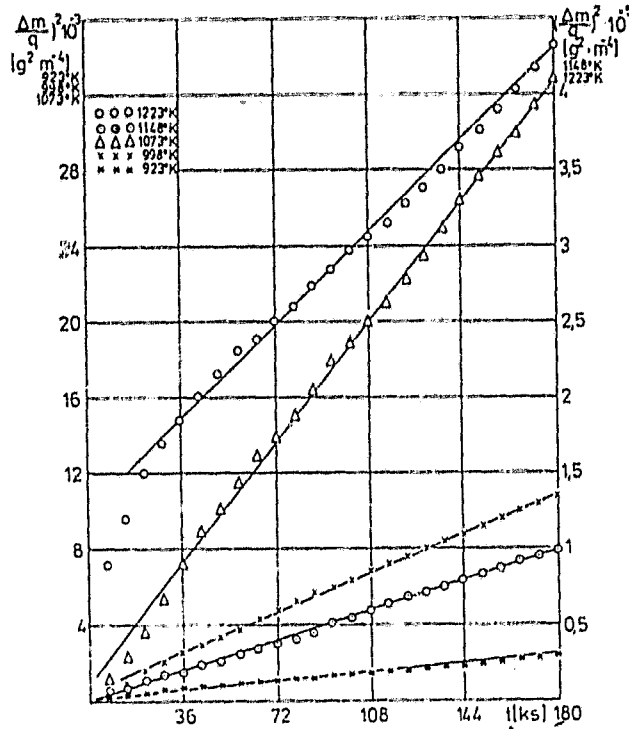* Numbers in margin indicate pagination in foreign text.

Figure 1. Parabolic course of the process of oxidation of two-component alloy containing 0.68% Al in the temperature range 923-1223 K (scales for temperatures 923, 998 and 1073 on the left side, and for 1148 and 1223 on the right side of graph)
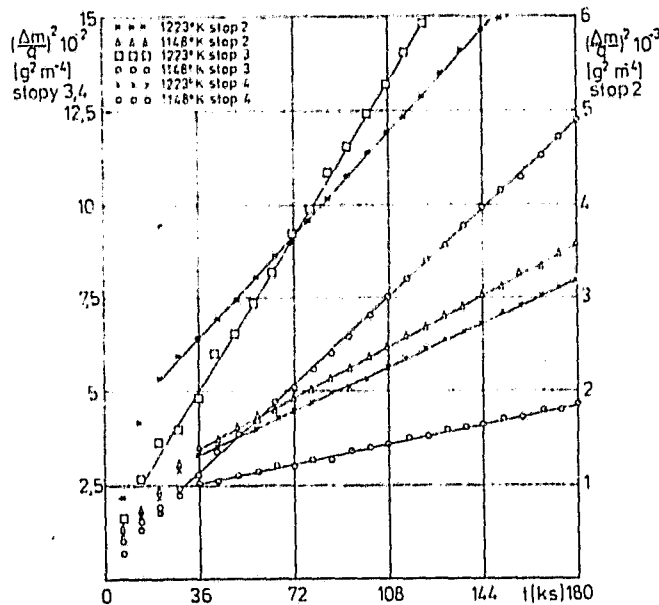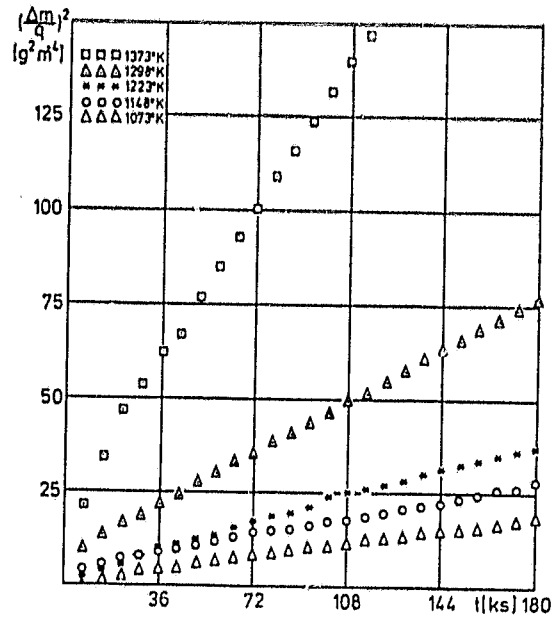

Figure 2. Parabolic course of the oxidation process of two-component alloys 2, 3, 4 and in the temperature range 1148-1223 K (scale for alloys 3 and 4 on the left, and for 2 on the right side of graph); stop = alloy, stop = alloys

Figure 3. Parabolic course of the oxidation of alloy 5 containing 18.08% Al in the temperature range 1073-1373 K.
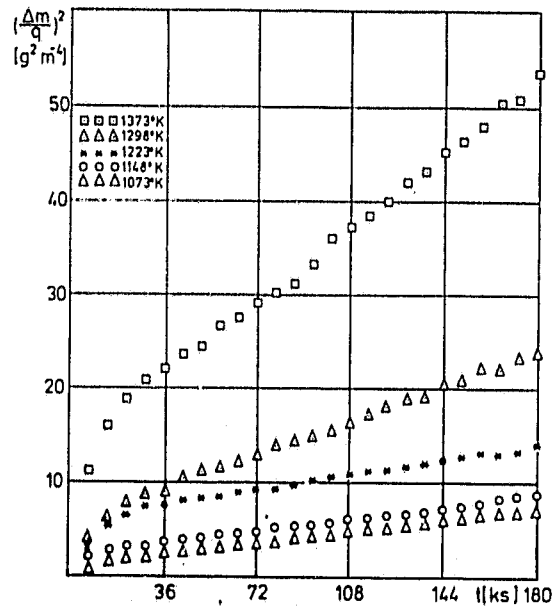

Figure 4. Parabolic course of the oxidation of alloy 6 containing 22.6% Al in the temperature range 1073-1373 K.

3

Studies of the oxidation rate

Kinetic studies were carried out on a thermogravimetric apparatus using the continuous isothermal gravimetric method. The rate of oxidation was measured during the 50-hour oxidation process at temperatures of 923, 998, 1073, 1148, 1223, 1298 and 1373 K in air atmosphere.

Errors in determining the parabolic reaction rate constant would arise from inaccuracies in directly measured quantities such as: time, mass and surface area of sample, and variations in temperature. The error resulting from inaccurate measurements of time, at the applied frequency of reacting every 10 minutes, was small and did not exceed 5 sec, and was 0.8% on the average. The accuracy of weighing did not exceed $\pm 5 \cdot 10^{-4}$ g, which at the total <u>/151</u> mass increases of about 0.1 g meant 1% error.

Dimensions of samples (disc of diameter 25 mm and average thickness 2.5 mm) were measured with an accuracy of about 0.01 mm; hence, the relative error of the measurement of surface of samples was 0.5%. The constancy of temperature was ensured by application of an automatic electronic compensator type EPP-120 with regulating attachment and continuous recording, of the degree of accuracy 0.5 and sensitivity 0.1% of the measuring range. It ensured the temperature stability within the limits ± 3 degrees, which corresponds to the maximum 0.5% error.

An error caused by changes of the metallic core surface during the reaction was also taken into account, following the work [2]. On the basis of average values obtained from seven measurements, graphs were prepared (Figures 1, 2, 3, 4, 5) showing the dependence of the square of mass increase of sample per unit area on the oxidation time. After no longer than 10 hours, one can see already

Table 1. Parabolic constants of the oxidation rate of Fe-Al alloys [$g^W/m^4 \cdot$ hour]

Alloy number	% Al	Temperature						
		923K	998K	1073K	1146K	1223K	1298K	1373K
1	0,68	62	200	617	1998	6000		
2	3,29	21	23	28	57	112		
3	7,2	4,7	11,3	11,7	24	44		
4	8,69	2	3	2,7	5	11,3		
5	18,08			0,32	0,45	0,65	1,42	3,9
6	22,60			0,12	0,14	0,16	0,32	0,83
7	29,88			0,22	0,31	0,39	0,01	2,30

the grouping of the majority of measurement points on a straight line, indicating that the process follows the parabolic law of oxidation. This regularity is particularly clear for alloys with lower contents of aluminum (below 18%), and is less pronounced for alloys with a higher percentage of aluminum (above 22%), which is connected probably with a larger measurement error arising for lower increases of the sample mass.

From straight-line portions of curves, we determined by a graphical method the rate constants of the reaction (Table 1). The mathematical analysis of the curves was performed on a digital
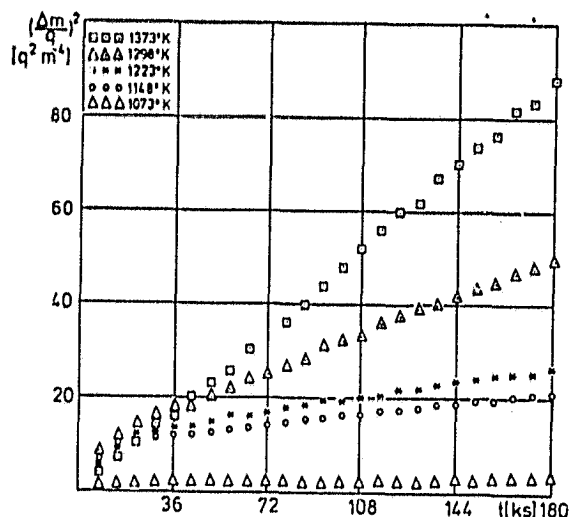
Figure 5. Parabolic course of the oxidation of alloy 7 containing 29.88% Al in the temperature range 1073-1373 K.

computer taking into consideration only the points obtained after 10 hours of the process. We tried to determine the probability that the points were following a parabolic relation by putting into a computer the values of the change of mass y and the duration of process x to fit the equation $y = ax^b + c$. The obtained values of b were in the range 0.5 ± 0.02. On the basis of these results we can accept, with probability 0.98, the hypothesis for the parabolic course of the process. Taking into account the mentioned values of the measurement errors, and the error connected with determining the parabolic constant [3], we assumed that the relative error did not exceed 10%.

Chemical X-ray microanalysis

A clarification of the oxidation process requires thorough studies of chemical and phase composition, and morphological structure of the product of oxidation. We determined local changes of chemical composition of the scale (burnout) and metallic base by using an electronic microprobe type IXA-3A. The X-ray microanalysis for the contents of iron and aluminum was performed on samples previously subjected to the oxidation process at the highest temperature for a given alloy. Two time periods of the oxidation process were
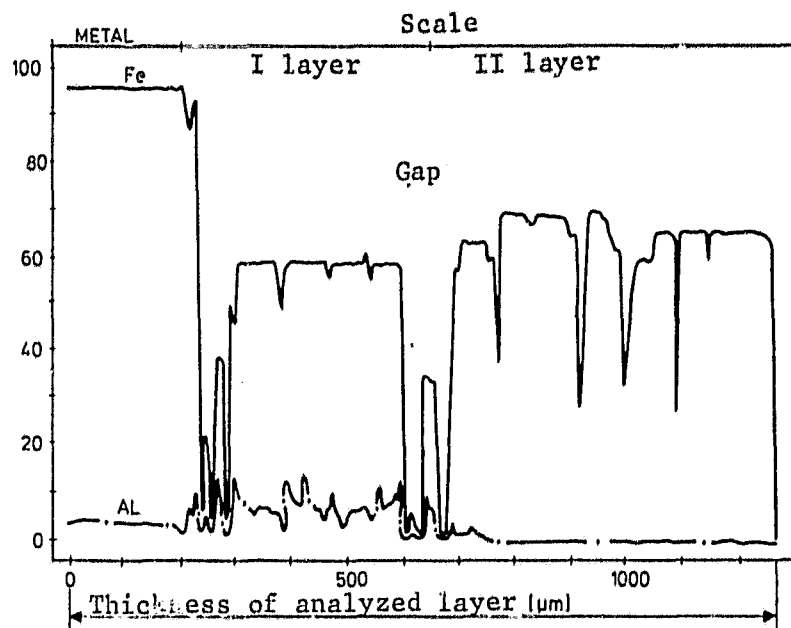
6

Figure 6. Distribution of the concentration of iron and aluminum in
scale and surface layer of alloy 2 with initial contents 3.78% Al.
Temperature of oxidation reaction 1223 K.

applied: 50 hours for samples of Fe-Al alloys containing up to   /154
7.2% Al, and 240 hours for samples with higher Al contents. The
results of X-ray microanalysis are presented here in the form of
graphs in Figures 6, 7, 8.

Alloys with low contents of aluminum up to 7.2%, oxidized
for 50 hours at a temperature of 1223 K, are covered with a scale
(burnout) composed of two distinct layers separated by a gap
(shown for illustration in Figure 6). The inside layer of the scale
shows a certain enrichment in aluminum in comparison with the metallic
base, whereas there is a lack of this components in the thicker outside
layer. Both in the first and the second layer, the dominant component
is iron. In the outside part of the scale, one can notice a sublayer
with reduced contents of iron. The surface-adjacent layer of metal
shows a slight increase of the aluminum contents towards the metal-
scale boundary. In the analyzed layer of metal, there are clear indic-
ations of an increase in the contents of aluminum with a concurrent
reduction of the contents of iron, which could be connected with
internal oxidation. The scale formed on the investigated alloys
18-30% aluminum is thin (up to 0.03 mm), forming one layer, and
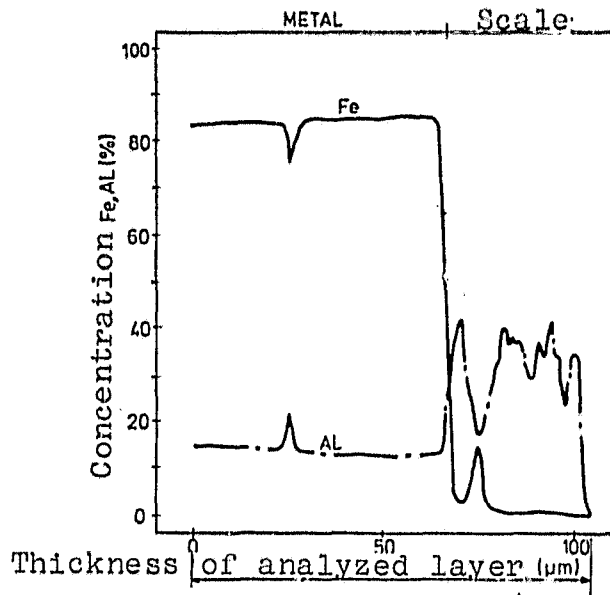consisting nearly exclusively of aluminum oxides (Figures 7 and 8).

Figure 7. Distribution of Fe and Al in scale and surface layer
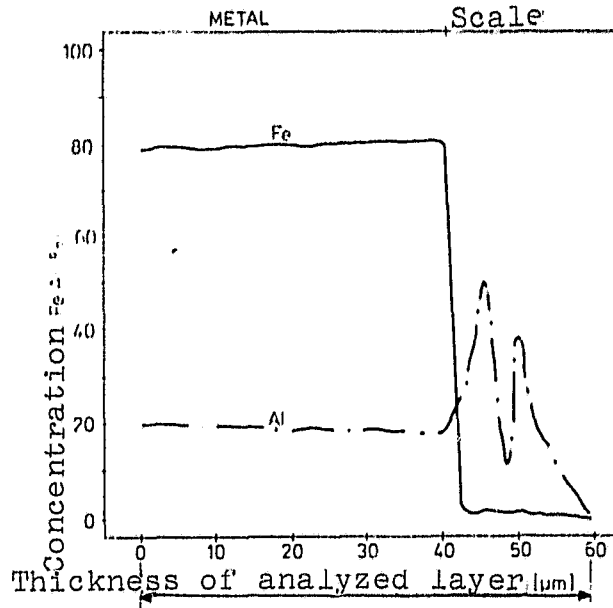of alloy 5 with initial content 18.08% Al. Oxid. temperature
1373 K.

Figure 8. Distribution of Fe and Al in scale and surface layer of
alloy 6 with initial content 22.6% Al. Oxid. temperature 1373 K.

In rare cases, for instance in alloy 5, one could notice traced amounts of iron oxides in the scale.

X-ray investigations

We performed an X-ray analysis using the powder method in order to identify the phase composition of the products of oxidation. Samples set aside for these investigations were sub-jected to oxidation using temperature and time, as in the case of studies with electronic microprobe. The results are presented in Table 2 (the data for identification of particular phases were taken from Reference [4]). It was found that the X-ray studies fully confirmed the results obtained with a microprobe. The scale formed on alloys containing up to 7.2% aluminum is composed nearly exclu-sively of iron oxides; the outside layer consists of hematite Fe_2O_3, magnetite Fe_3O_4 and wistite FeO, and the internal layer is composed of Fe_3O_4, FeO and mixed spinels $FeO \cdot Al_2O_3$, characteristic for alloys 2, 3, 4. The common characteristic feature for analyzed alloys of this group is the appearance of a wistite phase, in the case of alloy 1 - in the whole range of investigated temperatures, and in the case of remaining alloys - above the temperature 1073 K.

The scale formed on alloys containing 18-30% aluminum is composed of aluminum oxide, while iron oxides and spinels appear only in trace quantities. The dominant phase of Al_2O_3 in the scale varies depending on the oxidation temperature. At lower temperatures (up to 1223 K), the low-temperature type of $\gamma - Al_2O_3$ appears, whereas at temperatures above 1223 K the high-temperature type of $\alpha - Al_2O_3$ is formed, which is in agreement with the literature data [5, 6, 7].

Metallographic studies   /155

The morphological structure of the product of oxidation was studied using the microscopic metallographic analysis of a transverse polished side of the sample, made perpendicularly to the original surface of disc covered with scale. The analysis was supplemented

9

Table 2. Phase composition of oxide scales on
Fe-Al alloys.

Nr stopu	%Al	Temperature							
		923 K		1073 K		1148 K	1223 K		1373 K
		w	z	w	z	w	w	z	z
1	0,08	Fe_3O_4 FeOsl	Fe_2O_3 Fe_3O_4	FeO Fe_3O_4sl	Fe_2O_3 Fe_3O_4 FeO	...	FeO Fe_3O_4sl	Fe_2O_3 Fe_3O_4 FeO	
2	3,78	Fe_3O_4	Fe_2O_3 Fe_3O_4	Fe_3O_4 $FeO \cdot Al_2O_3$ FeOsl	Fe_2O_3 Fe_3O_4 $FeO \cdot Al_2O_3$ FeO	Fe_2O_3 Fe_3O_4	Fe_3O_4 $FeO \cdot Al_2O_3$ sl	Fe_2O_3 FeO Fe_3O_4	
3	4,70	Fe_2O_3 Fe_3O_4 $FeO \cdot Al_2O_3$sl		Fe_3O_4 $FeO \cdot Al_2O_3$	Fe_2O_3 Fe_3O_4	Fe_2O_3 Fe_3O_4 $FeO \cdot Al_2O_3$ FeO sl	Fe_3O_4 $FeO \cdot$ $\cdot Al_2O_3$sl	Fe_2O_3 Fe_3O_4 FeO	
4	7,20	$FeO \cdot Al_2O_3$ Fe_3O_4	$FeO \cdot Al_2O_3$ Fe_3O_4	Fe_2O_3 Fe_3O_4	Fe_2O_3 Fe_3O_4 $FeO \cdot Al_2O_3$ FeO sl	Fe_3O_4* $FeO \cdot Al_2O_3$ FeO $\alpha\text{-}Al_2O_3$sl $\gamma\text{-}Al_2O_3$sl	Fe_2O_3** $\alpha\text{-}Al_2O_3$ Fe_3O_4sl		
5	18,08	...		$\gamma\text{-}Al_2O_3$		...	$\alpha\text{-}Al_2O_3$ $\gamma\text{-}Al_2O_3$	$\alpha\text{-}Al_2O_3$ Fe_2O_3 sl	
6	22,60	..		$\gamma\text{-}Al_2O_3$			$\alpha\text{-}Al_2O_3$ $\gamma\text{-}Al_2O_3$	$\alpha\text{-}Al_2O_3$	
7	29,88			$\gamma\text{-}Al_2O_3$			$\alpha\text{-}Al_2O_3$ $\gamma\text{-}Al_2O_3$	$\alpha\text{-}Al_2O_3$ Fe_2O_3 sl	

w- internal layer of scale; * - phase composition of scale growth;
z- external layer of scale; ** - phase composition of scale between
outgrowths; sl - traces

10

with tests carried out by the marker method which gave some idea
about the relative role of reagents in the process of mass transport
through the layers of the reaction product. A platinum marker was
deposited on the polished surface of metal by spreading it in the
form of short sections, and subsequently by oxidizing this prepared
sample in the horizontal position. This is a method that ensures
the best results.

The scale formed on alloys containing up to 7.2% Al is well
delineated and consists of two distinct layers (Figures 9 and 10).
The marker is located in the external layer of the scale, somewhat
above the boundary with the internal layer. This fact indicates that   /156
the external layer of the scale is formed as a result of diffusion
of metal ions out from the core. At the same time, some oxide
exclusions are visible in the metallic phase, evidencing the
occurring phenomenon of internal oxidation (Figure 11).

The oxidation product found on the analyzed samples containing
18-30% Al is a deposited layer. Only at temperatures of 1373 K
is there a clear, thin scale, which forms a weakly adhering uniform
layer. Experiments carried out with the aid of platinum markers
failed to provide sufficient information with regard to the
direction of diffusion of reagents in the scale, since the thickness
of the scale obtained in 50 hours is of the order of 10-20 μm; hence,
is less than the marker diameter (about 50 μm). At higher temperatures
(above 1373 K), when thickness of scale increases, the marker is
destroyed [9, 10].

DISCUSSION OF RESULTS

The studies of the kinetics of the oxidation of two-component
Fe-Al alloys, and investigations of the chemical and phase composition
as well as structure of the scale, coupled with results of studies
of the diffusion of reagents obtained by the marker method, provided
information on the corrosion of these materials. On the basis of

11

External layer of scale

Platinum marker

Gap

Internal layer of scale

Metallic core

Figure 9. Microphotograph of a transverse polished side obtained on alloy 1 containing 0.68% Al. Temperature of oxidation 1223 K. Magnification 55 X

External layer of scale

Platinum marker

Cap

Internal layer of scale

Figure 10. Microphotograph of a transverse polished side obtained on alloy 2 containing 3.78% Al. Temperature of oxidation 1223 K. Magnification 75 X

12

results of kinetic studies of the oxidation process, conducted in the temperature range 923-1373 K, we can state that, at the most, after 10 hours the process follows a parabolic law, independently of the alloy composition and the reaction temperature. It means that the slowest step, determining the rate of reaction, is the diffusion of reagents in the solid phase of the product of reaction.

Figure 12 shows that the changes in reaction rates, as a function of the contents of aluminum in the investigated alloys, are partially similar for all temperatures. This similarity can be noticed clearly in the regions of two groups: alloys with low contents of aluminum - up to 7.2% and alloys with 18-30%. On the other hand, the composition of the alloy distinctly affects both the phase character (Table 2), morphological structure and thickness of the scale (Table 3). Because of these changes, we can divide alloys into two groups: alloys with low contents of aluminum up to 7.2% and alloys with higher contents of aluminum of 18-30%.

FE-Al alloys containing up to 7.2% Al

The dependence of the rate constant of the oxidation of Fe-Al alloys on the temperature is presented in semi-logarithmic form in Figure 12. The graphs show breaks which evidence the effect of temperature on the oxidation mechanism of the substance. In all the alloys containing up to 7.2% Al, one can see a distinct increase of the reaction rate as the temperature rises (above 1023 K for alloy 2, above 1073 K for alloy 3, above 1123 K for alloy 4). The authors think that this is connected with changes in the phase structure of the scale occurring at a temperature dependent on the contents of aluminum. As a result of these changes, the ratio of concentration of phases which form the composition of the internal layer of scale is a function of temperature for this group of materials. Namely, at temperatures of 1073 K and lower, the predominant phase in this layer is the spinel phase $Fe(Fe_{2-x}Al_x)O_4$, whereas at higher temperatures there appears also the wistite phase whose amount increases as the temperature rises (Table 2). In the light of kinetic studies and the
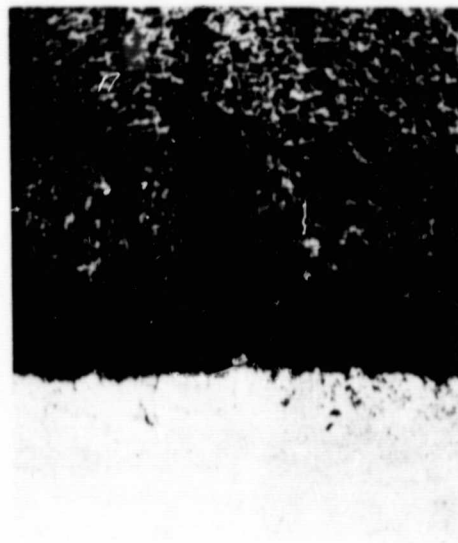
Figure 11. Microphotograph of a transverse polished side of near-surface layer of metallic core and scale, obtained on alloy 2 containing 3.78% Al. Temperature of the reaction of oxidation 1223 K. Magnification 350 X.
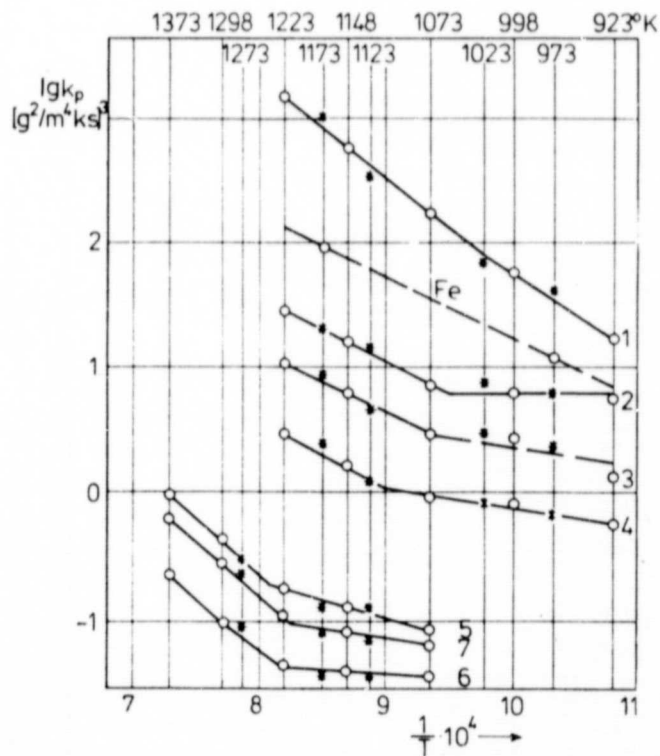

Figure 12. Dependence of the rate constant of oxidation reaction on the temperature for Fe-Al alloys.

14

results on the chemical and phase composition and morphological
structure of the scale, the following model for the oxidation
of these two-component alloys is proposed (Figure 13). At first,
a tri-layer scale characteristic for pure iron grows on the sur- <u>/160</u>
face of alloy, and at the same time oxidation of aluminum takes
place in the metallic phase. Growth of the external scale occurs
because of the out-of-core diffusion of ions and electrons of
iron, whereas the internal region of oxidation appears as a result
of the towards-the-core diffusion of oxygen through pores and
crevices formed in the scale. The source of oxygen for the process
of internal oxidation might as well be the dissociation of the
scale. As thickness of the scale increases, its contact with the
metallic core becomes interrupted in the second stage and a gap
is formed. In this way, conditions are created for dissociation
of the wistite layer and for secondary reactions of oxygen arising
from decomposition of FeO with iron ions coming from the metallic
phase. As a result, a porous internal layer of wistite is formed.
 In the discussed cases, the velocity of diffusion governs the rate
of growth of particular scale layers. Hence, one could conclude
that the wistite layer because of its thickness plays the decisive
role in the scale formation. The appearance of the wistite phase
in the scale is characteristic for the analyzed alloys oxidized
at temperatures above 1073 K.

Summing up the results pertaining to the kinetics and mechanism
of the oxidation of alloys 2, 3 and 4, we can state that the alloy-
ing additive, Al, decisively affects the rate of reaction and
chemical composition of the scale. This alloying additive
improves the heat resistance of the alloy and causes the formation
of a protective layer of spinel or oxide structure. The mobility
of ions of aluminum and in iron in the spinel phase is slower than
the mobility of iron ions in the wistite or even magnetite layer.

Fe-Al alloys containing 18-30% Al

Graphs of dependence of the rate constants of oxidation k_p on
temperature are shown in semi-logarithmic form in Figure 12.
The curves characterizing the high-aluminum alloys (5, 6,7)
show two straight lines with different slopes. The fact that this
dependence is not rectilinear throughout its entire course
but undergoes a break (change of slope) could be caused for two
reasons: either there are structural changes in the metallic
core itself, or there is a change in the phase composition of the
scale at temperatures close to the temperature corresponding
to the observed "break". If we accept as true the first alterna-
tive, i.e., the appearance of structural changes in the alloy,
then the break should be explained on the basis of the equilibrium
diagram of the Fe-Al system. We found on the basis of the X-ray
microanalysis that, during oxidation of high-aluminum alloys,
there is a selective oxidation of aluminum, which leads to im-
poverishment of this component on the external surface of the
metallic core (Figures 7,8), which is in agreement with the
literature data [11]. Such a reduction in the concentration of
aluminum could cause changes in the structure of surface-adjacent
layer of alloy. As the diagram of phase equilibria of the
system Fe-Al shows, in the range of concentrations 18-30% Al
there are two structures: one with ordering of the type Fe_3Al,
and the other of the type FeAl. These structures are
characteristic for temperatures lower then 973 K [1]. The
mentioned change of structure could affect the shape of the curve
only at temperatures lower than the analyzed ones. The observed
break in the curve characterizing a change in the oxidation rate
with change of temperature occurs in the temperature range 1223-1273K
(Figure 12). Under these conditions the possibility of structural
changes is not probable, and the explanation of the above "break"
based on the assumption of structural changes in the alloy is
problematic.

Table 3. Thickness of scale formed on surface of the oxidized Fe-Al alloys.

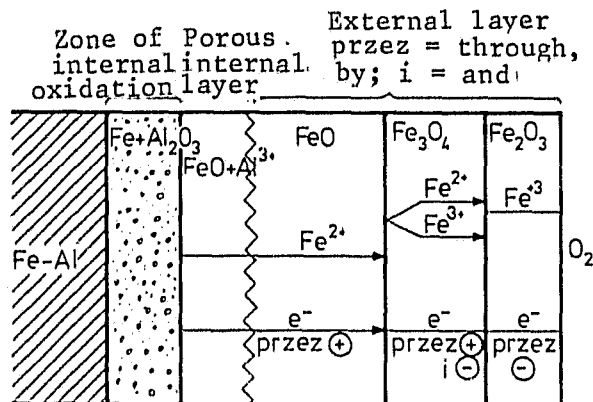| Type of alloy	%Al	Heating temperature, K	Time, hours	Thickness of scale		
				Internal	External	Total
1	0,68	1223	50	0,2	1,4 0,05	1,6-1,7
2	3,20	1223	50	0,5	0,6 0,1	1,2
3	7,42	1223	50	0,05	0,05	0,1
4	8,69	1223	100	0,05	0,11	0,16
5	18,08	1373	240	—	—	0,03
6	22,6	1373	240	—	—	0,02
7	29,88	1373	240	—	—	0,01

Figure 13. Diagram of the mechanism II of the formation of heterophase multilayer scale on the analyzed two-component Fe-Al alloys containing up to 7.2% Al.
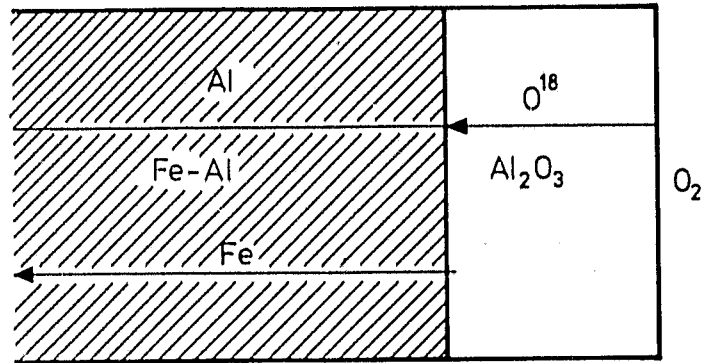
Figure 14. Mechanism for the formation of an oxide scale on
the analyzed high-percent Fe-Al alloys, on the basis
of the author's investigations (directions of dif-
fusion of the reagents were taken on the basis of
Reference /15/).

17a

It remains, therefore, to consider the second assumption
that changes in phase composition of the scale are responsible
for the "break" occurring on the curve (Figure 12). A change
of the phase composition of the scale may be caused by the appearance
of new phases or by phase change of the reaction product [13, 14].
The X-ray structural studies of scale formed on analyzed alloys
have shown (Table 2) that in a layer formed at the temperature
1373 K there are trace amounts of iron oxides in addition to the
basic phase $\alpha-Al_2O_3$. But at the temperature 1073 K, the presence
of iron oxides was not observed (Table 2), and the basic layer
of the scale is formed by aluminum oxides at the phase $\gamma - Al_2O_3$.
The reason for a change of the oxidation rate with the rise of
temperature may be, therefore, either the appearance of iron
oxides at higher temperatures or a phase transition of aluminum
oxides. It does not appear probable that iron oxides appearing
in trace amounts could cause such a distinct change in the activa-
tion energy (Figure 12). It seems, therefore, highly probable
that the appearance on the surface of the oxide $\alpha-Al_2O_3$ which   /162
has a higher activation energy than the oxide $\gamma - Al_2O_3$, is a
factor accelerating the oxidation process.

On the basis of the results of these studies, supplemented by
the literature data concerning the directions of diffusion of
reagents [15], we offer the following model of the formation mechanism
of the scale on alloys analyzed (Figure 14). In the first stage
of reaction, crystalline embryos are formed, probably of both oxides –
iron and aluminum. The possibility of the formation of aluminum
oxide is, however, larger than of the hematite layer, since the
absolute value of the free energy of formation of aluminum oxides
is considerably greater than that of iron oxides. The contents
of aluminum are considerable; hence in a short time the whole
surface of metal becomes covered with a uniform dense layer of
aluminum oxides. The formed layer of Al_2O_3, having nearly no de-
fects, has considerable resistance to both the out-of-core dif-
fusion of cations of two metals and to into-the-core diffusion of

18

gaseous oxygen [16]. For these reasons, the thickness of the scale increases only little under these conditions.

CONCLUSIONS

1. The oxidation of all the investigated Fe-Al alloys occurs after passing the initial stage (up to 10 hours), according to the parabolic kinetic law, indicating that the total oxidation process is governed by the process of diffusion. Kinetics of the oxidation process of alloys heated in air atmosphere depends on the temperature and composition of the alloy, the rate of reaction decreasing with the higher percentage contents of aluminum.

2. The dominant component of the scale on alloys containing up to 7.2% Al is iron, and on alloys containing 18-30% Al - aluminum. In the case of alloys with low contents of Al, we find also aluminum oxides in the metallic phase, formed in the process of internal oxidation. As the content of aluminum in the alloy increases, spinels appear in the scale, and with a still further increase of aluminum they turn into oxides - γ-Al_2O_3 and α -Al_2O_3. A layer of spinels or aluminum oxides slows down the process of oxidation.

19

REFERENCES

[1]   H. Przewlocka, J. Siedlecka, Archiwum Hutnictwa, Vol. 23, 109, (1978)

[2]   J. Romanski, Doctoral dissertation, AGH, Krakow 1963

[3]   J. Siedlecka, Doctoral dissertation. Polit. Czestochowska, Czestochowa 1976.

[4]   I. J. Mirkin. Handbook for X-ray analysis of polycrystals (in Russian). Moskwa 1961.

[5]   L. Atlas, K. Sumida. J. Amer. Ceram. Soc. Vol. 41, 150 (1950)

[6]   P. Pepin, L. Tartian. Metal. Corr. Ind. Vol. 36, 140 (1961).

[7]   J. Trillat, L. Tartian, P. Pepin. Metal Corr. Ind. Vol. 36, 133 (1961)

[8]   S. Mrowiec, Werber: Modern heat resistant (refractory) materials, Katowice 1971.

[9]   W. Markiewicz, J. Podhorodecki, Zesz. Nauk. AGH Matematyka-Fizyka-Chemia, Vol. 20, 43, (1974)

[10]   M. Cirlip, B. Krasilov, V. Vladomirov, A. Bialobzeski. Zascita Metallov, Vol. 9, 478, (1973).

[11]   R Grace, A. Seybolt, J.Electrochem. Soc. Vol. 105, 582, (1958)

[12]   K. Sckowski, J. Pkastowski. Atlas of structures of normalized cast alloys, Warszawa 1972.

[13]   W. Hagel. Corrosion, Vol. 21, 316 (1965)

[14]   F. Saegusa, L. Lee. Corrosion, Vol. 22, 168, (1966)

[15]   S. Mrowiec, T. Werber. Modern heat resistant (refractory) materials. Warzawa 1968.

[16]   G. Ervin. Acta Crystallogr., Vol. 5, 103 (1952)