Corrosion of Pure Metals in Molten Vanadium Pentoxide*

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Synopsis
A study was made of the corrosion behavior of iron, cobalt, zirconium, titanium, nickel, and chromium in V₂O₅ melt. Three types of oxidation laws were found: accelerated, linear, and logarithmic. Linear rate laws at the initial stage and the causes of the accelerated oxidation of iron and cobalt in V₂O₅ melt were discussed.

I. Introduction
It is well known that severe corrosion of heat-resisting alloys occurring in boilers and gas turbines is caused by the reaction with molten ash produced by the combustion of heavy oils. Vanadium pentoxide and the complex sodium vanadates in the oil-ash have been found to possess "catastrophic" corrosive properties.

Although many investigations¹⁻⁻¹⁵ have so far been made on the oil-ash corrosion of heat-resisting alloys, the characteristics, the cause, and the mechanism of the corrosion have not been fully understood owing to the complicated corrosion conditions and the difficulty in reproducing reliable results. The methods of test and the mechanism of oil-ash corrosion have been summarized by Miyagawa et al.¹⁷

Knowledge of the corrosion mechanism of metals in molten vanadium pentoxide, which has been hardly investigated, is of importance in deriving the mechanism of the oil-ash corrosion. Recently, Pantony and Vasu¹⁷ carried out the original investigation to make clear the corrosion mechanism of metals. The accelerated oxidation mechanism, however, could not be made clear.

In the present work, the corrosion of selected single metals in the presence of molten vanadium pentoxide was investigated in order to make clear the mechanism of the accelerated oxidation and obtain the basic data on the oil-ash corrosion of heat-resisting alloys.

II. Experimental Procedure
1. Materials
Vanadium pentoxide used was of G. R. grade. Metals used were as follows:

(1) Iron, containing main impurities (in wt%): 0.02C, 0.003Si, 0.003Mn, 0.007P, and 0.005S
(2) Cobalt, having nominal purity of 99.57wt% and containing main impurities (in wt%) : 0.005S, 0.009C, 0.194Fe, 0.110Ni, 0.028Si, and 0.012Mn
(3) Nickel, having nominal purity of more than 99.5wt%
(4) Zirconium, prepared from zirconium sponge containing impurities (in wt%): 0.0304Fe, 0.0094Hf, 0.0060Mg, 0.0051Mn, 0.0057Ni, 0.0085Si, 0.0148Ti, 0.0057V, 0.0056C, and 0.0020N
(5) Titanium, prepared from titanium sponge containing impurities (in wt%): 0.016Fe, 0.081Cl, 0.005N, tr. Al, 0.0003Cr, 0.035Mg, 0.001Mn, 0.007Si, tr. V, 0.025O, 0.019C, and 0.0023H
(6) Electrolytic chromium, containing (in wt%): 99.2Cr, 0.11Fe, 0.009Al, 0.029N, 0.5O, 0.006H, 0.01Si, 0.02C, 0.002P, 0.027S, 0.001Cu, and 0.002Pb

The discs of the metals, about 1.5 mm thick and 8 mm diameter, were polished with emery paper through 4/0 grade and degreased in benzene.

2. Corrosion Studies
The oxidation rates were measured by using the thermobalance assembly, shown in Fig. 1. The specimen was placed on the bottom of a cylindrical silica crucible and covered with the requisite amount of vanadium pentoxide. The crucible was suspended by a platinum wire from the beam of balance and put in the position A in the reaction tube. After the sufficient amount of oxygen, air or oxygen–nitrogen mixture, dried and free from CO₂, was passed through the reaction tube, the crucible was pulled up to the center of the furnace kept at a fixed temperature, and then the measurement was started.

Fig. 1. Thermobalance assembly
III. Results and Discussion

1. Oxidation Process

The oxidation process of metal in V$_2$O$_5$ melt can be considered to consist of several sequential process presented schematically in Fig. 2.

Stages (1) and (10) can be regarded as chemical reaction between oxidizing gas and V$_2$O$_5$ melt. Stages (2) and (9) will primarily depend on the physical properties, such as viscosity and density, of V$_2$O$_5$ melt. Stages (3) and (8) will be dependent on the physical and chemical properties of both V$_2$O$_5$ melt and corrosion products. The diffusion rates of oxidizing agents and metal ions will be influenced by composition and viscosity of the melt. Stages (4) and (6) are diffusion process of ions in the solid corrosion products. The products generally consist of metal oxides and/or metal vanadates and their physical morphologies (for example: degree of compactness, size and distribution of pore) will be complicated and greatly affect the diffusion rate of ions. When the scale is very porous and does not prevent the penetration of the melt, the diffusion will be not retarded. Stage (7) represents the dissolution of the corrosion products into V$_2$O$_5$ melt. At high temperature V$_2$O$_5$ melt can dissolve most of metal oxides. The rate of dissolution may well depend on the physical and the chemical properties of the corrosion products. At the initial stage of the oxidation or in the formation of porous corrosion products, stage (5) represents the oxidation reaction between metal and V$_2$O$_5$. When the corrosion products are compact, stage (5) represents the phase boundary reaction between corrosion products and metal. In either case, the reaction will depend on the chemical properties of the metal, and the nature of surface and the impurities of specimens.

When the rate-controlling stage is stage (1) or (10), the oxidation rates may well be virtually independent of the depth of the melt and the nature of the metal. If any of the stages (2), (3), (8), or (9) is rate-controlling, the process is likely to be diffusion-controlled with relatively low activation energy corresponding to that of the diffusion in the melt, and the oxidation rates may well be virtually independent of the nature of the metal.

It is at the final stage of the oxidation progress that stage (4) or (6) is rate-controlling. In this case, the activation energy is expected to be relatively high and the oxidation rate to be very low.

If stage (5) is rate-controlling, the activation energy will take large value and the reaction rate will be independent of the depth of melt, concentration of oxidizing agents and the nature of the corrosion products.

When the oxides formed are compact and refractory for the melt, stage (7) will proceed with the very slowed rate.

2. Oxidation Rate

The oxidation rates of metals in V$_2$O$_5$ melt at temperatures from 700° to 900°C in 1 atm oxygen were shown in Figs. 3 to 6. Three types of oxidation behavior were found as shown in Table 1. (a) Accelerated Oxidation (Type A)

The oxidation of iron and cobalt obeyed the linear rate law at the initial stage. At 800° to 900°C, in the following stage the oxidation was accelerated and then retarded at the final stage, while at 700° and 750°C the accelerated oxidation was less remarkably observed.

![Fig. 3. Corrosion of iron with molten V$_2$O$_5$ in oxygen atmosphere](image)

![Fig. 4. Corrosion of cobalt with molten V$_2$O$_5$ in oxygen atmosphere](image)
(b) Linear Oxidation (Type L)

The oxidation of zirconium obeyed the linear rate law. It is noted that the oxidation of titanium was considered to obey the linear rate law and the oxidation behavior was rather complicated because the specimen moved upwards in the melt at the stage following the initial linear process. Chromium was the most corrosion-resistant of all the metals investigated, and its oxidation rate was too low to be determined by the present method.

3. Linear Rate Law at the Initial Stage

The oxidation of iron, cobalt, zirconium, and titanium at the initial stage was found to obey the linear rate law, and the mechanism of this linear process will be discussed.

The oxidation reaction of metal M in V₂O₅ melt can be expressed formally as follows:

\[ 2V^{3+} + 5O^{2-} + M(s) = 2V^{4+} + 4O^{2-} + MO(s) \]  

Metal oxide, MO(s), formed dissolves in V₂O₅ melt,

\[ MO(s) = M^{2+} + O^{2-} \]

tetrapvalent vanadium ion V⁴⁺ is reoxidized at the melt/gas interface.

\[ 2V^{4+} + \frac{1}{2}O_{2}(g) = 2V^{5+} + O^{2-} \]

The oxidation of metal shown by Eq. (1) can proceed thermodynamically under the conditions where the oxidation of V⁴⁺ [Eq. (3)] does not proceed; in pure nitrogen, for instance. It is clear from the fact that the equilibrium oxygen partial pressure of vanadium oxides (VO₂-V₂O₅ system) is considerably high compared with that of other metal oxides. But, the oxidation rate in pure nitrogen will be very low.

The rate-controlling process at the initial stage will be: (i): the oxidation of the metal [Eq. (1)], (ii): dissolution of the metal oxide in V₂O₅ melt [Eq. (2)], (iii): the diffusion of oxidizing agent through almost pure V₂O₅ melt, and (iv): the oxidation of V⁴⁺ ion with oxygen gas [Eq. (3)]. The processes (i) and (ii), being a sort of chemical reactions at high temperature, will proceed very fast, and the process (iv) will be strongly affected by P₀₂.

Figure 7 shows the model of process (iii), which is rate-controlled by the diffusion of the oxidizing agent. Provided that the melt is not oxidizing in itself, the flux of oxidizing agent through the melt is a measure of the oxidation rate (or weight loss) of the metal, being equal to the rate of increase in weight, \( dW/dt \). Under steady-state conditions, from Fick’s first law,

\[ \frac{dW}{dt} = S \cdot D_s \cdot \frac{C_1 - C_2}{l - l'} = S \cdot D_s \cdot \frac{C_3 - C_4}{l'} \]

where \( D_s \) and \( D_b \) are the diffusion coefficients of the oxidizing agent in V₂O₅ melt and V₂O₅–MO melt, respectively, and \( S \), surface area of the specimen, was regarded to be equal to the cross-sectional area of the vessel. Assuming that the concentration of the oxidizing agent in the melt in equilibrium with the metal

\[ C_1^* \text{ and } C_2^* \text{ : equilibrium concentration of oxidizing species between gas and V}_2\text{O}_5 \text{ melt, and between V}_2\text{O}_5-\text{MO melt and metal, respectively} \]
is negligibly small \((C_2^+\approx0)\), then from Eq. (4),
\[
\frac{dW}{dt} = \frac{D_0(C_2^+-C_2)+D_bC_z}{S} dt
\]
On condition that at \(t=0\), \(W=W_0\) and integrating from \(t=0\) to \(t=t_1\), then,
\[
W_t-W_0 = JW = \frac{D_0(C_2^+-C_2)+D_bC_z}{S} t
\]
provided that \(S\), \(D_0\), \(D_b\), \(C_z^+\), and \(C_2\) are independent of time \(t\).

At the initial stage \(V_2O_5\)-MO melt layer is very small in thickness and regarded to be the boundary layer. Provided that \(l'\approx0\), then,
\[
JW = \frac{D_0C_z^+}{S}t
\]
Equation (7) shows that the oxidation obeys the linear rate law and the oxidation rate is independent of the nature of metals and inversely proportional to the depth of melt. The effect of depth of \(V_2O_5\) melt on the oxidation behavior of iron was shown in Fig. 8. It was found from this result that (1): the decrease in the depth of melt increases the oxidation rate at the initial stage, (2): in the following stage, regardless of the depth of melt, the accelerated oxidation occurred, and (3): as the depth of melt decreased, the oxidation rate began to fall in a short time (at the final stage).

The initial linear rate constants for the oxidation of iron, cobalt, titanium, and zirconium at 850°C were plotted against the reciprocal depth of melt in Fig. 9. The plots were linear, demonstrating inverse proportionality between the rate constant and the depth of melt. It is noted that the rate constants for iron and cobalt are approximately twice as large as those for titanium and zirconium.

Figure 10 shows that the temperature dependence of rate constants obeys an Arrhenius-type equation,
\[
k = A_1 \exp\left(-\frac{E_1}{RT}\right)
\]
\(\frac{dW}{dt} = \frac{D_0C_z^+}{S}t
\]

The activation energy \(E\) and the frequency factor \(A\) are shown in Table 2. The mean value of \(E\) is calculated to be 23.6±1.5 kcal/mol excluding the rather high value for zirconium. The activation energy for the diffusion of the oxidizing agent in PbO melt, a typical ion conductor, obtained from the variations of oxygen potential measured by using a solid electrolyte, \(ZrO_2\cdotCaO\), was 18 kcal/mol.\(^{18}\) On the other hand, the activation energy for the diffusion obtained from the viscosity of \(V_2O_5\) melt was 13.2 kcal/mol. This difference is considered to be as follows. \(C_2^+\) and \(D_0\) in Eq. (7) are represented by

\[
C_2^+ = A_1 \exp\left(-\frac{E_1}{RT}\right)
\]
\(D_0 = A_2 \exp\left(-\frac{E_2}{RT}\right)
\]

From Eqs. (7) to (10),
\[
k = A_1A_2 \exp\left(-\frac{E_1+\frac{E_2}{R}}{T}\right)
\]

It follows from Eqs. (8) and (11) that \(E=E_1+E_2\). Generally, \(C_2^+\) increases with the temperature, so

![Fig. 8. Effect of depth of \(V_2O_5\) melt on the corrosion of iron (850°C, in air)](image)

![Fig. 9. Effect of depth of \(V_2O_5\) melt on the corrosion rates of metals at 850°C](image)

![Fig. 10. Relation between \(\log k\) and \(1/T\) \((l=4\ mm)\)](image)

| Table 2. Activation energy \(E\) and frequency factor \(A\) for oxidation of metals with \(V_2O_5\) in 1 atm oxygen |
|-----------------|-----------------|-----------------|
| Metal           | This work        | Panyoni, et al.\(^{17}\) |
|                 | \(E\) (kcal/mol) | \(A\) (kcal/mol) |
| Iron            | 24.8            | 1.8×10⁴          | 21.2               |
| Cobalt          | 24.2            | 2.0×10⁴          | 27.0               |
| Zirconium       | 29.9            | 7.3×10⁴          | —                  |
| Titanium        | 22.2            | 4.3×10⁵          | 24.0               |
$E_1 > 0$. Then, the activation energy for the oxidation is considered to take the value high by $E_1$ compared with that for the diffusion. Some convection of melt seems to increase the oxidation rates, considering the size of the specimen and the vessel. The present discussion has been made on the diffusion-controlled process, but it can not explain the facts that the oxidation rates depend on metals. In such a case, it is also suggested to treat the process as mixed controlling with both diffusion and reaction rates. This treatment is confined to discuss the process qualitatively and considered to be less successful. Thus, it is suggested that the differences of the linear rate constants are ascribable to the differences in the effects of metals on (i): the rates of oxidation of metals [Eq. (1)], (ii): the rates of dissolution of metal oxides [Eq. (2)], and (iii): the convection in the melt. The increase of the oxidation rate and the enhancement of convection due to the rise of temperature caused by the exothermic oxidation reaction of the metal will be described later.

4. Accelerated Oxidation Phenomenon

The oxidation behavior of A type metal, such as iron and cobalt, is characterized by the accelerated oxidation. The causes of the accelerated oxidation are investigated.

1. Temperature Changes by Oxidation of Metal and Dissolution of Metal Oxides

The oxidation reaction of metal is, in general, exothermic. The rise of temperature due to the reaction is expected to be measured in this process. The discs about 10 mm diameter x 20 mm of iron, cobalt, and zirconium were dipped in about 15 g of $V_2O_5$ melt in the silica crucible, and the variations of temperature of the specimens and the melts were measured. In the case of iron, A type metal, the rise of temperature of 10°C or more were observed in both specimen and melt in 5 min after dipping. The rise of temperature was also observed in the case of cobalt, but not in the case of zirconium, L type metal. The dissolution of Fe$_2$O$_3$ and CoO in $V_2O_5$ melt was confirmed to be endothermic. From the above-mentioned fact, it is inferred that the rise of temperature consequent on the exothermic oxidation increases the oxidation rate and enhance the convection in the melt.

2. Physical Properties of $V_2O_5$-MO Melt

The accelerated oxidation may be caused by the variations in the physical properties of $V_2O_5$ melt due to containing dissolved metal oxides. For example, (a): the decrease in density of the melt near the surface of specimen, and (b): lowering of viscosity of the melt may enhance the convection and oxidation rate.

The density of melts of systems $V_2O_5$-Fe$_2$O$_3$, $V_2O_5$-CoO, $V_2O_5$-NiO, and $V_2O_5$-ZrO$_2$ was investigated. It was found that the density of the melts increased with the additions of metal oxides. The viscosity of $V_2O_5$ melt was reported to increase with the additions of Fe$_2$O$_3$. Electric conductivity of $V_2O_5$ melt generally increases by the addition of Fe$_2$O$_3$, its variation being fairly complicated. Conductivity of ionic conductor depends on the diffusion rates of ions. But, in the case of $V_2O_5$ which is semiconductor the increased conductivity does not directly result in the increase of diffusion coefficient.

From the above-mentioned results of density, viscosity and electric conductivity of $V_2O_5$-MO melts, it is less reasonable to conclude that the diffusion coefficient of oxidizing agent increases and the convection in $V_2O_5$ melt enhances as the metal oxides dissolves into the melt.

3. Effect of Addition of Metal Oxides on Oxidation Rate

The constitution of the melt varies by dissolving the oxidation products, which will affect the oxidation rate. Figure 11 shows the oxidation of iron in $V_2O_5$-Fe$_2$O$_3$ melts. In the melts containing 0 to 10 mol% Fe$_2$O$_3$, the initial oxidation rate increased by the addition of Fe$_2$O$_3$ and the accelerated oxidation occurred. On the other hand, in the melts with Fe$_2$O$_3$ content of 15 mol% or more, the initial rate decreased with increasing Fe$_2$O$_3$ content and the accelerated oxidation was not observed. Figure 12 shows the initial rate constants of iron in $V_2O_5$-Fe$_2$O$_3$ melts, cobalt in $V_2O_5$-CoO melts, nickel in $V_2O_5$-NiO melts, and...
zirconium in $V_2O_5-ZrO_2$ melts as ratio to that of each metal in pure $V_2O_5$ melt in connection with $V_2O_5-MO$ binary diagrams. From Fig. 12 it follows that the effects of the additions of metal oxides are closely connected with three types of the oxidation behavior previously mentioned, namely:

1. The oxidation rates of iron and cobalt, A type metal, reaching a maximum at the eutectic composition. (It has been found that the oxidation rate of metals in $V_2O_5-Na_2SO_4$ melts reached a maximum at $Na_2SO_4$ content of 10 mol%, which corresponded the eutectic composition.)

2. The oxidation rate of zirconium, L type metal, hardly depends on the compositions of $V_2O_5-ZrO_2$ melts.

3. The oxidation rate of nickel, D type metal, decreases greatly by the addition of nickel oxide.

Cunningham and Brasunas showed that the amount of oxygen absorbed in $V_2O_5-Na_2SO_4$ melts was maximum in the most corrosive in their composition. Although the sort of the oxidizing agent in $V_2O_5$-MO melts has not been made clear, its concentration is considered to be connected with the concentration of dissolved oxygen in the melts and increases with the dissolved Fe$_2$O$_3$ or CoO. If that is the case, the results shown in Fig. 12 can be explained satisfactorily.

Thus the causes of the accelerated oxidation can be suggested to be (1): the increase of the oxidation rate and the enhancement of convection in the melt due to the rise of temperature by exothermic oxidation reaction of the metal, and (2): the increase of concentration of oxidizing agent in $V_2O_5$-MO melt.

**IV. Conclusions**

The linear relationship at the initial stages implies that the oxidation reaction is mainly diffusion controlled. The causes of the accelerated oxidation of iron and cobalt in $V_2O_5$ melt can be suggested to be the rise of temperature and the increase of concentration of oxidizing agent in $V_2O_5$-MO melt.

**REFERENCES**

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