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Fluxing of protective oxide scales on superalloys via a thermal surface tension gradient

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An oxide fluxing model involving continuous dissolution and reprecipitation of oxide scales via a thermal surface tension effect is postulated to explain hot corrosion of high teperature alloys and coatings in gas turbines. It is demonstrated that due to the existence of a thermal surface tension gradient, a molten alkali salt film condensed on a turbine vane or blade can undergo a circulating flow motion. A cycle of oxide dissolution at the hot end of the molten salt film and reprecipitation at its cold end can thus be established continuously to remove the protective oxide scales from the surfaces of the turbine components. Under gas turbine operating conditions, the liquid salt film can flow at a velocity as high as 1.5 cm $\sec^{-1}$, and the oxide scale can be continuously fluxed away at a rate over 1.5 mg $cm^{-2}h^{-1}$ ($\sim$5 microns per hour for Al_2O_3). This can, therefore, be one of the mechanisms to sustain hot corrosion, especially under conditions where large surface temperature gradients are encountered.

1. Introduction

The mechanisms of hot corrosion of high temperature alloys and coatings used in combustion turbines have been the subject of many studies. In recent years, the chemical fluxing model for hot corrosion, first proposed by Bornstein and DeCrescente [1] and later expanded by Goebel and Pettit [2] and Goebel *et al.* [3], has attracted considerable attention. This model postulates that the dissolution of the protective oxide scales on alloy surfaces (mainly Al_2O_3 and Cr_2O_3) in molten alkali sulphate (e.g. Na_2SO_4, binary Na_2SO_4–$CoSO_4$, etc.) is responsible for the onset of accelerated hot corrosion. According to the basicity of the alkali sulphate melt, the oxide scales can be dissolved via two types of reactions:

(a) Acidic dissolution at high SO_3 partial pressures and low oxygen ion activities; e.g.

$$Al_2O_3 + 3Na_2SO_4 \rightarrow \underline{Al_2(SO_4)_3} + 3Na_2O \quad (1)$$

and,

(b) Basic dissolution at low SO_3 partial pressures and high oxygen ion activities, e.g.

$$Al_2O_3 + Na_2SO_4 \rightarrow \underline{2NaAlO_2} + SO_3 \quad (2)$$

(In Equations 1 and 2, the underlined species represent those dissolved in Na_2SO_4 melts.)

A schematic diagram of the gas/melt/oxide/alloy system is shown in Fig. 1. If the protective oxide scale is dissolved, the metal substrate is rendered unprotected and thus prone to catastrophic attack by the corrosive environment. However, once the melt is saturated with oxide, further oxide dissolution will not occur. To sustain hot corrosion, a mechanism by which the dissolved oxide is continuously transported away from the dissolution site and reprecipitated at another site is required. Based on this requirement, Rapp and Goto [4] suggested that a negative gradient of oxide solubility at the oxide/salt interface is necessary to sustain the dissolution/reprecipitation process. Recently, Shores [5] has used this criterion along with the oxide solubility–melt basicity relationship determined by Gupta and Rapp [6] to show that basic dissolution (with negative oxide solubility gradient) can lead to fluxing, but generally, with a few possible exceptions, acidic dissolution (with zero or positive oxide solubility gradients) cannot when the acidic component is

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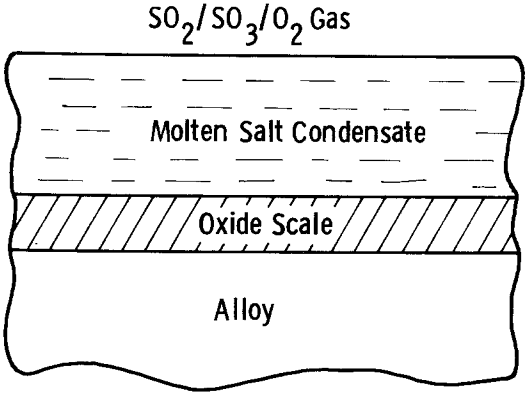

Figure 1 Schematic diagram of the gas/salt/oxide/alloy system.

supplied in the gas phase. Due to this constraint, together with the fact that usually only very small concentration gradients are believed to exist in the salt film [5], the oxide fluxing by molten salt condensate is still not well understood [5, 7]. In this paper, another oxide fluxing mechanism, based on continuous dissolution and reprecipitation of oxides via a thermal surface tension gradient effect is postulated and discussed.

Since the platforms of turbine blades are usually cooled, a temperature gradient, sometimes as large as several hundred degrees centigrade from blade root to blade tip, can exist on the blade surface. A molten salt film condensed on the blade surface, therefore, encounters a thermally induced surface tension gradient along its free surface. According to recent surface tension measurements on Na_2SO_4 melts [8], a temperature difference of 10° C results into a surface tension difference of 0.6 dyne cm^{-1}. The tangential stress resulting from this surface tension difference will cause the molten salt surface to flow in the direction of increasing surface tension (from high to low temperature for Na_2SO_4 melt) as shown in Fig. 2. Since the movement of the molten salt will also be accompanied by a viscosity shear stress as well as a pressure gradient stress, it is shown in the following section that the interaction of these stresses forces the molten salt film to undergo a circulating flowing motion with the upper salt layers flowing towards the cold end, and the lower layers flowing towards the hot end.

Since the solubility of Al_2O_3 or Cr_2O_3 are functions of temperature, the liquid salt that reaches the low temperature end will be in a state of supersaturation; there will, therefore, be a driving force to reprecipitate the extra oxide. When the liquid salt returns to the hot end, the oxide in it will be below the saturation limit, and thus more oxide will be dissolved in the melt. A cycle of oxide dissolution at the hot end and reprecipitation at the cold end will, therefore, be established. This cycle can sustain hot corrosion in a way very similar to that suggested by Rapp–Goto model [4] based on the oxide solubility gradient considerations. However, the suggested mechanism is not restricted by the sign of the oxide solubility gradient across the salt film thickness, and can, therefore, explain both the acidic and the basic fluxing.

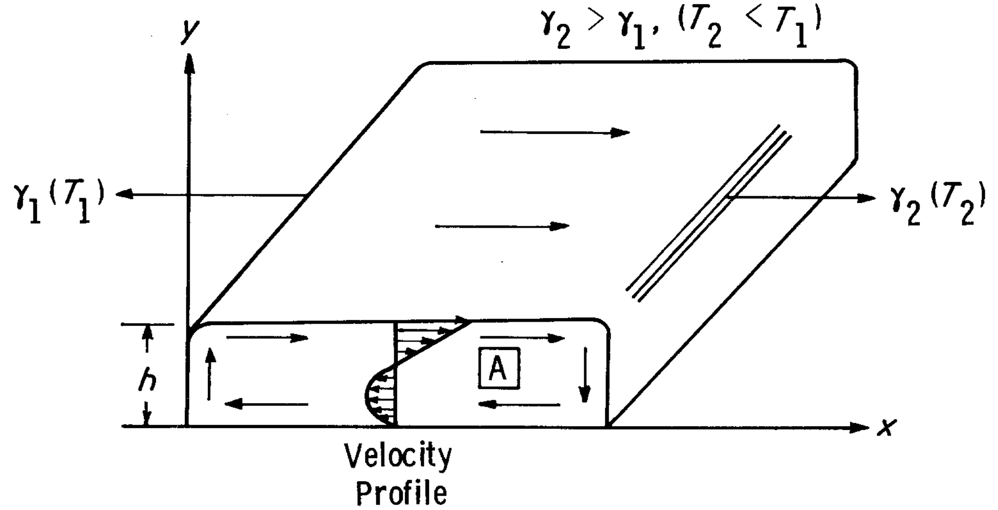

Figure 2 Schematic diagram showing the motion of molten salt film under the action of a thermal surface tension gradient (γ = surcace tension; T = temperature).

2. Mathematical derivation of the molten salt flow pattern

Fig. 2 shows a schematic diagram representing a molten salt film with unit length and width and a thickness of h. Assuming that the temperature gradient exists only in the x-direction, a surface tension gradient, $d\gamma/dx$, will be generated in the direction opposite to that of the temperature gradient for the Na_2SO_4-based melts. (For some liquids, such as $PbO-B_2O_3-SiO_2$ ternary melts, that exhibit the very unusual phenomenon of increasing surface tension with increasing temperature, $d\gamma/dx$ and dT/dx will be in the same direction.) Under the action of this surface tension gradient, the molten salt film will tend to move in the x-direction (increasing surface tension) with a local velocity determined by the vertical distance above the melt basal plane. Since the flow under consideration is viscous in nature, a viscous shear stress gradient in the direction perpendicular to the flow direction, $d\tau/dy$, as well as a fluid pressure gradient along the direction of the flow, dp/dx, will also be encountered [9].

Considering a free body of molten salt in the form of an elementary cube of volume $\Delta x \Delta y \Delta z$, (Fig. 3), the only stresses that need to be considered for the motion in x-direction are the viscous shear stresses acting upon the $\Delta x \Delta z$ surfaces and the fluid pressure stresses acting upon the $\Delta y \Delta z$ surfaces. For steady state flow, the summation of forces in the x-direction should be zero; i.e.

$$\Sigma F_x = \left(\frac{d\tau}{dy}\Delta y\right)\Delta x\Delta z - \left(\frac{dp}{dx}\Delta x\right)\Delta y\Delta z = 0 \tag{3}$$

Therefore:

$$\frac{d\tau}{dy} = \frac{dp}{dx}. \tag{4}$$

Since the viscous shear stress τ can be easily expressed as a product of the viscosity coefficient μ and the velocity gradient dV_x/dy [10], it follows from Equation 4 that

$$\frac{d}{dy}\left(\mu\frac{dV_x}{dy}\right) = \frac{dp}{dx}. \tag{5}$$

If μ is assumed to be constant for convenience, Equation 5 can be integrated to give,

$$\mu\frac{dV_x}{dy} = \frac{dp}{dx}y + c \tag{6}$$

where c is a constant. At the salt film surface (at $y = h$), the viscous shear stress balances the surface tension stress; i.e.

$$|\tau|_{y=h} = \left|\mu\frac{dV_x}{dy}\right|_{y=h} = \frac{d\gamma}{dx}. \tag{7}$$

Combining Equations 6 and 7:

$$c = \frac{d\gamma}{dx} - \frac{dp}{dx}h. \tag{8}$$

Substituting Equation 8 into Equation 6 and integrating, one obtains that

$$V_x = \frac{1}{\mu}\left[y\frac{d\gamma}{dx} + \left(\frac{y^2}{2} - yh\right)\frac{dp}{dx}\right]. \tag{9}$$

The relationship between $d\gamma/dx$ and dp/dx can be derived by using the fact that the net volume flux across the $y-z$ plane is zero, i.e.

$$\int_0^1 \int_0^h V_x dy dz = 0 \tag{10}$$

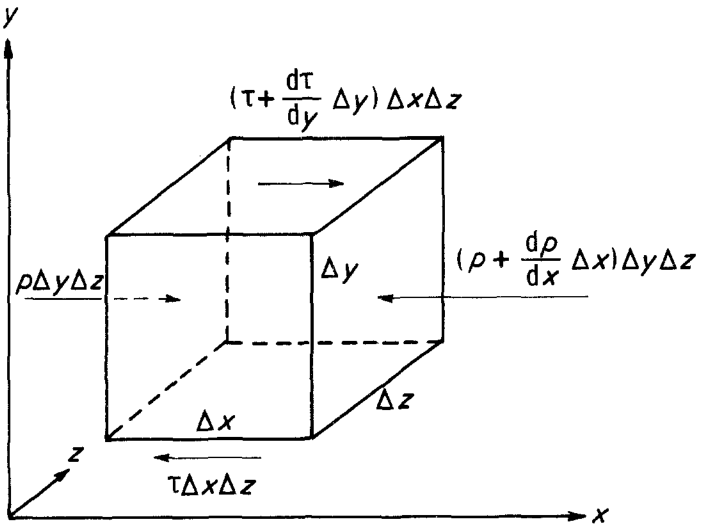

Figure 3 Sketch of fluid pressure and shear on elementary cube A.

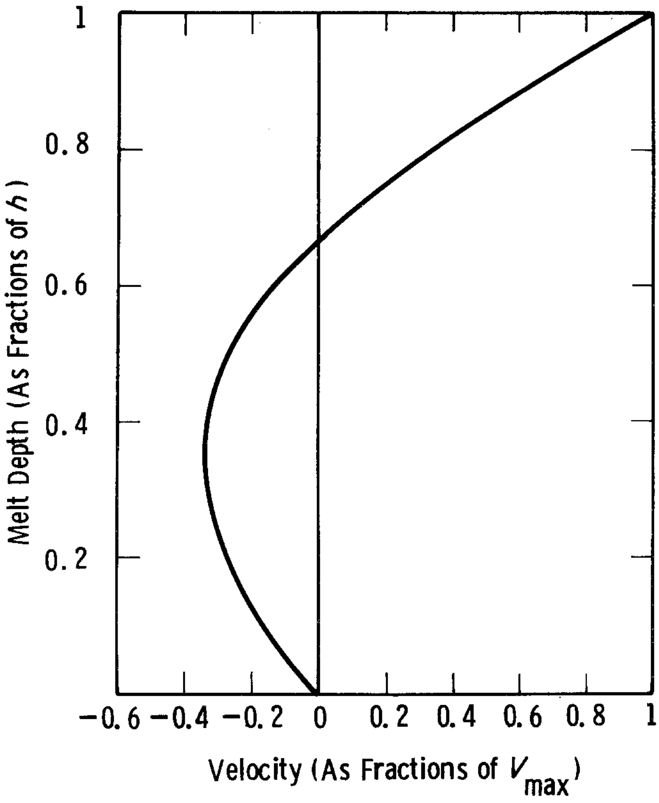

Figure 4 Velocity profile of melt as a function of melt depth.

and therefore:

$$\frac{\mathrm{d}p}{\mathrm{d}x} = \frac{3}{2h}\frac{\mathrm{d}\gamma}{\mathrm{d}x}. \tag{11}$$

The equation for the local flow velocity of the molten salt film can therefore be expressed by combining Equation 11 with Equation 9, as

$$V_x = \frac{1}{\mu}\left(\frac{3y^2}{4h} - \frac{y}{2}\right)\frac{\mathrm{d}\gamma}{\mathrm{d}x} \tag{12}$$

or, in terms of the temperature gradient, as

$$V_x = \frac{1}{\mu}\left[\frac{3y^2}{4h} - \frac{y}{2}\right]\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x}. \tag{13}$$

The velocity profile as a function of the vertical distance from the basal plane is plotted in Fig. 4. The maximum velocity occurs at the surface of the molten salt (at $y = h$) with a magnitude of

$$V_{\max} = \frac{h}{4\mu}\frac{\mathrm{d}\gamma}{\mathrm{d}x} = \frac{h}{4\mu}\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x}. \tag{14}$$

It can also be seen that at the location of $y = (2/3)h$, the velocity profile experiences an inversion where the velocity changes its direction from positive to negative. This velocity profile demonstrates that the flow pattern is a circulating one with the top layers of the molten salt flowing towards the low temperature end, and the lower layers flowing towards the high temperature end. This phenomenon of liquid circulation induced by thermal surface tension gradient (called Marangoni flow [10]) has been studied by fluid mechanics researchers in the motion of bubbles in molten glasses and other liquids [10–13].

3. Application of surface tension induced liquid flow to oxide scale fluxing kinetics

To obtain the magnitude of circulating velocity expected for the salt film on gas turbine components, consider a molten alkali sulphate thin film (e.g. Na_2SO_4 or a mixed sulphate with a lower melting point) with a thickness of 0.01 cm covering an area 1 cm x 1 cm. Depending on the type and design of gas turbine and the location of the turbine blade at which this molten salt film is condensed, it can encounter different magnitudes of surface temperature gradients varying from about 10 to over $100^\circ\mathrm{C\,cm^{-1}}$. For illustration purposes, using the following values,

$$h = 0.01\ \mathrm{cm}$$

$$\frac{\mathrm{d}T}{\mathrm{d}x} = -100^\circ\mathrm{C\,cm^{-1}}$$

$$\frac{\mathrm{d}\gamma}{\mathrm{d}T} = -6 \times 10^{-5}\,\mathrm{N\,m^{-1}\,{}^\circ C^{-1}}\ [8]$$

and

$$\mu = 1 \text{ centipoise*}$$

it is calculated from Equation 14 that the surface of the molten salt film can flow at a maximum velocity of 1.5 cm sec^{-1}. Even at locations with smaller (10° C cm^{-1}) temperature gradient, the melt surface can still flow with a rather high velocity of 0.15 cm sec^{-1}.

To estimate the rate (R) at which the molten salt can circulate between the hot and the low temperature ends, V_x is integrated over the y- and z-axes between the limits of $y = 0$ to $(2/3)h$ and $z = 0$ to 1: i.e.

$$R(\text{cm}^3\,\text{sec}^{-1}) = \int_0^1 \int_0^{\frac{2}{3}h} V_x \mathrm{d}y \mathrm{d}z. \qquad (15)$$

Assuming that μ does not vary with y and z, it is calculated that the molten salt film with a 100° C cm^{-1} temperature gradient can circulate at a rate as high as 2.2×10^{-3} cm^3 sec^{-1} (4.4 mg sec^{-1} for Na_2SO_4). The molten salt film under consideration having a volume of 0.01 cm^3 (20 mg) will take only about 4.5 sec for the total volume of salt to be transported through one cycle.

If the solubilities of Al_2O_3 or Cr_2O_3 in the molten salt as functions of temperature are known, the rate at which the oxide scales can be continuously fluxed away by this mechanism can be readily determined. For the purposes of illustration, a value of 1 ppm° C^{-1} for the solubility gradient is assumed in the temperature range of interest. Further, assuming that oxide dissolution and reprecipitation are not rate controlling and that all the supersaturated oxide is condensed at the cold end, it is calculated that an Al_2O_3 or Cr_2O_3 scale underneath the 1 cm^2 salt condensate can be continuously removed at a rate as high as $4.4 \times 100 \times 10^{-6}$ mg cm^2 sec^{-1} (~ 1.5 mg cm^{-2} h^{-1}). For an Al_2O_3 scale with a density of about 3 g cm^{-3}, this fluxing rate is equivalent to 5 μm h^{-1}. At locations with only 10° C cm^{-1} temperature gradient, the corresponding fluxing rate would be 0.015 mg cm^{-2} h^{-1}. Although this rate is one hundred times smaller than that for locations with the higher temperature gradient, it is still about the same order of magnitude as the oxide scale growth rate encountered by gas turbine superalloys and coatings in oxidation environments.

In the above derivations, only temperature gradients, not actual melt temperatures, have been specified. An important assumption, however, is that the temperature is high enough for the alkali sulphate melts to be in their molten state. Since this mechanism requires the existence of a temperature gradient, it is not applicable to isothermal hot corrosion conditions prevailing, for example, in laboratory tests.

4. Conclusions

It is demonstrated that due to the existence of a thermal surface tension gradient, a condensed liquid sulphate salt film on combustion turbine vanes and blades can undergo a circulating flow motion. With the upper liquid salt layers flowing towards the cold end and the bottom layers flowing towards the hot end, a cycle of oxide dissolution and reprecipitation can be established to remove continuously the protective oxide scales formed on high temperature alloys and coatings. It is illustrated that the maximum velocity of the liquid salt surface can be as fast as 1.5 cm sec^{-1}, and the oxide scale can be continuously removed at a rate over 1.5 mg cm^{-2} h^{-1}; this mechanism can, therefore, sustain hot corrosion. Since both the salt film flow velocity and the oxide removal rate are proportional to the temperature gradient across the length of the salt film, this mechanism could be specially important for situations with steep temperature gradients.

While this mechanism seems attractive in explaining sustained hot corrosion, some further questions need to be explored. These questions relate to the magnitude of supersaturation required for the reprecipitation of the dissolved oxide; the relative magnitude of the rates of oxide dissolution and reprecipitation and the molten salt circulation rate; and the likelihood of the reprecipitated oxide particles to become suspended in the melt and flowing along with it instead of depositing near the cold end. Experimental studies are required to answer these questions. Other factors, such as the effects of dissolved oxide, impurities, and surface contaminants on the melt surface tension, and the influence of temperature

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*μ of molten alkali sulfates are not available; however, A. Klemm mentions in "Molten Salt Chemistry", edited by M. Blander (Interscience Publishers, New York, 1964) that the viscosities of molten salts are in the order of that of water (~ 1 centipoise).

gradients in the y- and z-directions on the flow pattern, also need to be investigated. This model is only a first attempt to take the salt motion into consideration in explaining hot corrosion, and these additional complicating factors will be the subject of future investigations.

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