

## Reaction of Cobalt in Ar-SO<sub>2</sub> Atmospheres at 500–900°C

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*The attack of cobalt by sulfur and oxygen simultaneously in Ar-SO<sub>2</sub> atmospheres in the temperature range 500–900°C has been found to conform to the pattern established by the attack of other metals under similar conditions. A thermodynamic and kinetic interpretation of the mechanism has been proposed. The results also indicate that during the initial stages sulfur diffuses through the initially formed oxide layer, eventually leading to formation of the commonly observed duplex sulfide and oxide scale.*

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**KEY WORDS:** cobalt; oxidation; sulfidation; conjoint attack.

### INTRODUCTION

Although a certain amount of work has been carried out on the sulfidation, oxidation, and sequential sulfidation and oxidation of cobalt and its alloys,<sup>1–5</sup> there has been little systematic and reproducible work<sup>6–8</sup> on the simultaneous attack of sulfur and oxygen on cobalt at high temperatures in atmospheres containing sulfur dioxide.

Konev<sup>9</sup> *et al.* oxidized cobalt in atmospheres containing SO<sub>2</sub> and CO<sub>2</sub> at 1050, 1120, and 1190°C, and reported that the scale consisted of one phase, CoO, and that the oxidation kinetics followed a parabolic rate law, the rate constant of which increased with the partial pressure of SO<sub>2</sub> in the atmosphere. It was also suggested that sulfur dissolves in cobalt as anions on anion sites, the solubility increasing with the SO<sub>2</sub> partial pressure. The solution mechanism increased cation vacancy concentrations and thereby enhanced cation diffusion, increasing the parabolic rate constant. Alcock<sup>10</sup> *et al.*

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exposed nickel, copper, iron, and cobalt to  $\text{SO}_2\text{-O}_2$  atmospheres in the ratio 2:1 at  $688^\circ\text{C}$  and found the cobalt specimen to be covered by a thin layer of  $\text{CoS}$  next to the metal, surmounted successively by a thicker layer of  $\text{CoO}$  followed by a thin layer of  $\text{CoSO}_4$ . Birks and co-workers<sup>11,12</sup> and Rahmel and Gonzales<sup>13</sup> studied the joint attack of sulfur and oxygen on iron, copper, and nickel and alloys with chromium. It was shown that in these cases the increase in the reaction rate is mainly due to sulfide formation at the scale-metal interface, or within the scale layer, or to joint oxide and sulfide formation at the scale-gas interface. These workers have also provided evidence for sulfur dissolution in the oxide. Liquid scales have been observed at higher temperatures consisting of metal-sulfide and sulfide-oxide eutectics, leading to increases in reaction rates due to the faster diffusion through the liquid scales. Pettit *et al.*<sup>14</sup> and Birks<sup>15</sup> have examined the thermodynamic conditions that can arise during the simultaneous attack of metal and alloys by oxygen and another oxidant. For the case of oxygen and sulfur they have concluded that the activity of sulfur at certain reaction sites of high metal activity can exceed that required for sulfide formation. This is true particularly during early stages of the reaction or at the scale-gas interface. Similarly  $\text{SO}_2$  can penetrate a protective sulfide-free oxide scale, leading to sulfide formation within the oxygen scale at sites of sufficiently high metal activity, where the oxygen activity is low, i.e., especially at the metal-scale interface.

In the present study, the scaling of pure cobalt in  $\text{Ar-SO}_2$  gas mixtures has been studied in the temperature range  $500\text{-}900^\circ\text{C}$ .

## EXPERIMENTAL

Standard disk specimens, 12 mm in diameter and 3 mm thick, were cut from hot-rolled cobalt bar of at least 99.5% purity (the major impurity being 0.4% nickel). Specimens were wet ground on 600 grade paper to remove surface scratches and then cleaned with acetone to remove grease and dirt before starting each experiment. Experiments were carried out in the temperature range  $500\text{-}900^\circ\text{C}$  in  $\text{Ar-2\%SO}_2$  and  $\text{Ar-10\%SO}_2$  atmospheres in the same manner as described by Flatley and Birks<sup>11</sup> and Wootton and Birks.<sup>12</sup> Reaction kinetics were followed using an automatic recording thermobalance. Reactions were started by rapidly heating the specimens in the established atmosphere and terminated by cooling rapidly at the end of the experiment.

Oxidized specimens were prepared for optical metallography and electron probe microanalysis. X-ray diffraction analysis of the scale was used to identify reaction products and SEM examination was used to study surface topography.

## RESULTS

The kinetic data for the oxidation of cobalt over the temperature range 500–900°C in atmospheres containing Ar-2%SO<sub>2</sub> and Ar-10%SO<sub>2</sub> are shown in Figs. 1 and 2, respectively. At all temperatures an initial constant

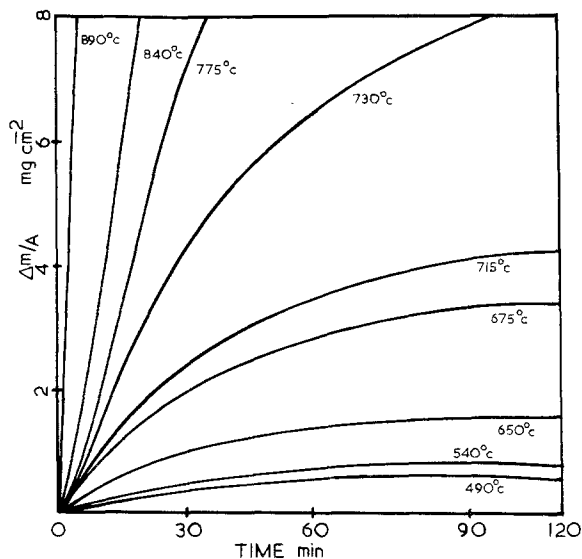


Fig. 1. Scaling kinetics of cobalt in Ar-2% SO<sub>2</sub>.

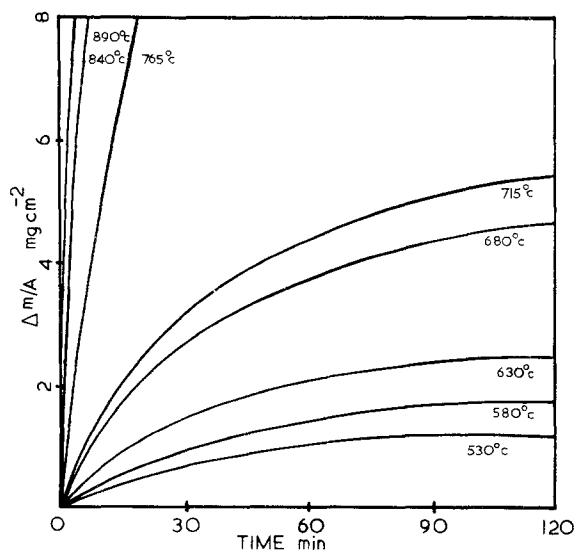


Fig. 2. Scaling kinetics of cobalt in Ar-10% SO<sub>2</sub>.

rate period is followed by a decreasing rate period. The initial constant reaction rate increases with increase in temperature and sulfur dioxide concentration in the gas stream. The initial constant rate may also be found to increase with the gas flow rate.

### Metallographic Features

#### 680–780°C

At temperatures of 680–780°C the scale formed consists of a thin layer of cobalt sulfide,  $\text{Co}_9\text{S}_8$ , next to the metal, surmounted by a thick duplex layer composed of cobalt oxide ( $\text{CoO}$ )–cobalt sulfide ( $\text{Co}_9\text{S}_8$ ). Experiments terminated after about 5 min, i.e., shortly after the specimen had reached the reaction temperature, confirmed that both the sulfide layer and the duplex layer form early in the reaction. Typical features of the scale are shown in Fig. 3 for a specimen interrupted at the end of the constant rate period. Figure 4 for a specimen exposed for 2 hr shows that the sulfide layer next to the metal has hardly thickened, whereas the duplex thickness has increased with time. In this temperature range the duplex structure formation persists for at least 2 hr.

#### 500–680°C

At temperatures of 500–680°C structures similar to those observed in the temperature range 680–780°C are found with the addition of a very fine duplex layer formed near the scale–metal interface.

Experiments carried out at 840°C, close to the Co– $\text{Co}_9\text{S}_8$  eutectic point (873°C), show very rapid scale growth with metallographic features similar to those reacted at 780°C. The scale at the specimen corners, shown in Fig. 5,

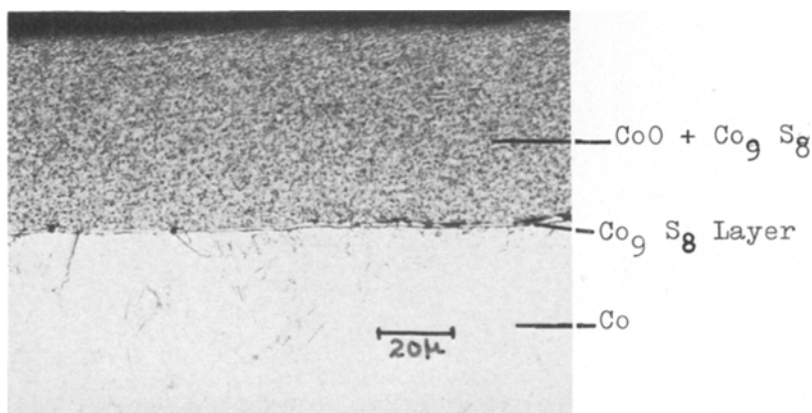


Fig. 3. 30 min in Ar–2%SO<sub>2</sub> at 780°C.

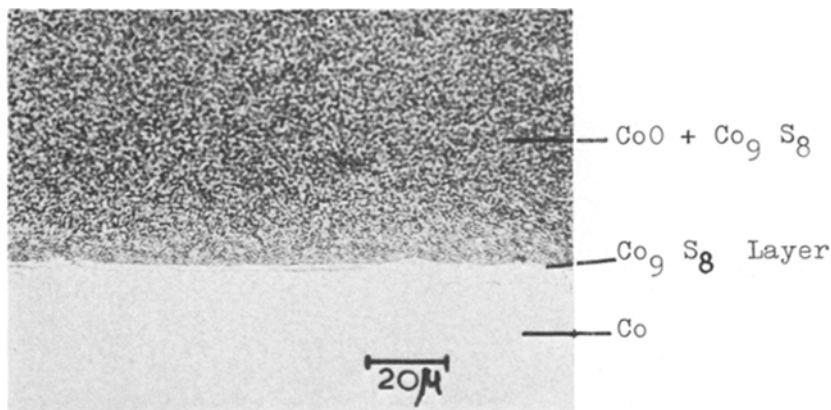


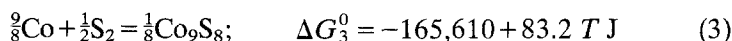
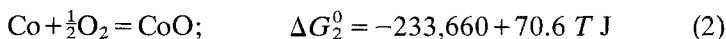
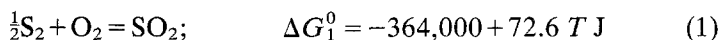
Fig. 4. 120 min in Ar-2%SO<sub>2</sub> at 780°C.

gives evidence of substantial scale plasticity and inward movement to maintain scale-metal contact even after 2 hr.

At 900°C, above the Co-Co<sub>9</sub>S<sub>8</sub> eutectic point, the reaction product adjacent to the metal appears to have been liquid and is covered by an oxide-sulfide duplex. The sulfide layer next to the metal has penetrated down the grain boundaries as shown in Fig. 6.

## DISCUSSION

The relevant reactions in the system cobalt-oxygen-sulfur are



Cobalt oxide is expected to form at all temperatures because the oxygen partial pressure is governed by the impurity oxygen pressures in the argon gas stream at  $10^{-5}$ – $10^{-6}$  atm.

Cobalt sulfide is only expected to form when the local sulfur partial pressure generated is greater than the equilibrium sulfur partial pressure for sulfide formation. From Eq. (1), the local sulfur pressure generated is given by

$$p'_{\text{S}_2} = (p_{\text{SO}_2}/p_{\text{O}_2})^2 \cdot \exp(2\Delta G_1^0/RT) \quad (4)$$

The sulfur partial pressure in equilibrium with Co<sub>9</sub>S<sub>8</sub> is given by Eq. (3) as

$$p_{\text{S}_2}^+ = (1/a_{\text{Co}}^{9/4}) \cdot \exp(2\Delta G_3^0/RT) \quad (5)$$

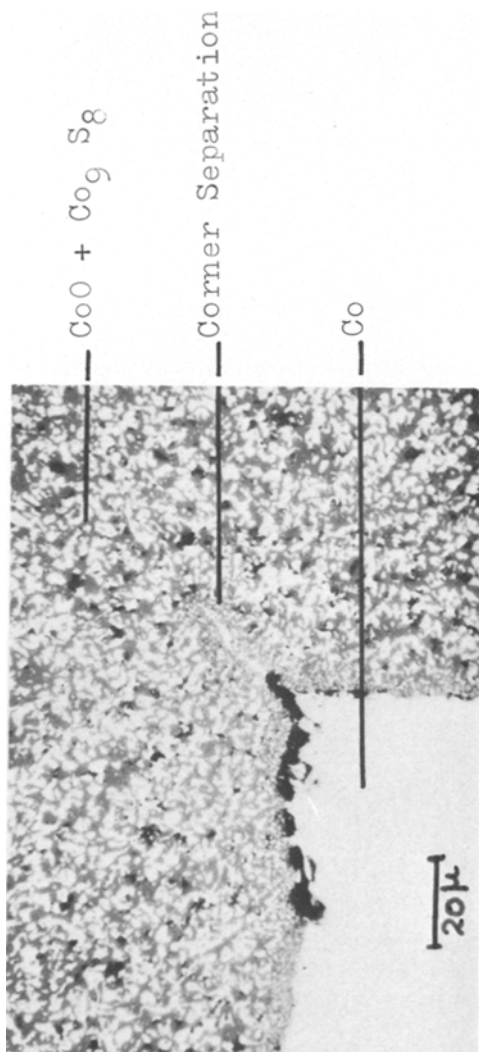


Fig. 5. 30 min in Ar-2%SO<sub>2</sub> at 840°C.

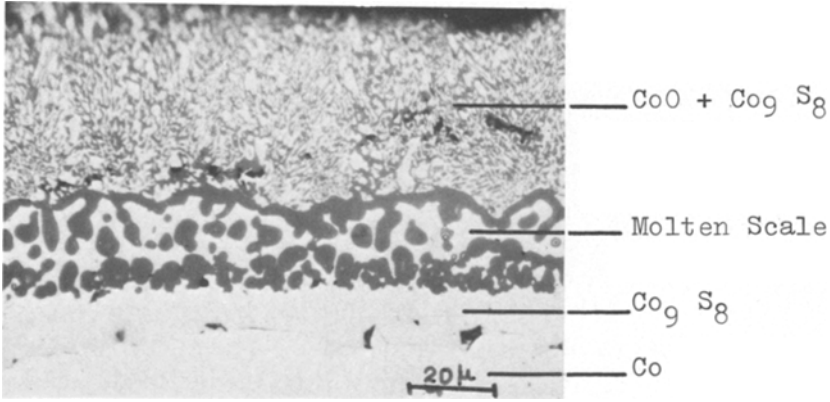


Fig. 6. 30 min in Ar-2%SO<sub>2</sub> at 900°C.

The condition for sulfide formation at or within the oxide is

$$p'_{S_2} > p_{S_2}^+ \tag{6}$$

Substituting the values of ( $p'_{S_2}$ ) and ( $p_{S_2}^+$ ) from Eqs. (4) and (5) into Eq. (6), we get

$$(p_{SO_2}/p_{O_2})^2 \cdot \exp(2\Delta G_1^0/RT) > a_{Co}^{-9/4} \cdot \exp(2\Delta G_3^0/RT)$$

or

$$a_{Co}^{9/4} \cdot (p_{SO_2}/p_{O_2})^2 \cdot \exp[2(\Delta G_1^0 - \Delta G_3^0)/RT] > 1 \tag{6a}$$

Assuming that the local oxygen partial pressure at any site is controlled by the relevant cobalt activity applied to the equilibrium of Eq. (2), Eq. (6a) reduces to

$$a_{Co}^{25/8} \cdot p_{SO_2} \cdot \exp(\Delta G_1^0 - 2\Delta G_2^0 - \Delta G_3^0/RT) > 1 \tag{7}$$

Substituting the appropriate free energy values in Eq. (7) the conditions for simultaneous sulfide and oxide formation can be found. The activity of cobalt necessary to form a duplex scale according to Eq. (6) is given in Table I for different SO<sub>2</sub> partial pressures.

Table I. Critical Cobalt Activities for Sulfide Formation

$p_{SO_2}$ , atm	Temperature, °K				
	700	800	900	1000	1100
1	$1.24 \times 10^{-4}$	$7.98 \times 10^{-4}$	$3.38 \times 10^{-3}$	$1.07 \times 10^{-2}$	$2.77 \times 10^{-2}$
$10^{-1}$	$2.60 \times 10^{-4}$	$1.66 \times 10^{-3}$	$7.06 \times 10^{-3}$	$2.23 \times 10^{-2}$	$5.79 \times 10^{-2}$
$10^{-2}$	$5.40 \times 10^{-4}$	$3.48 \times 10^{-3}$	$1.47 \times 10^{-2}$	$4.66 \times 10^{-2}$	$1.2 \times 10^{-1}$
$10^{-3}$	$1.13 \times 10^{-3}$	$7.27 \times 10^{-3}$	$3.08 \times 10^{-2}$	$9.75 \times 10^{-2}$	$2.52 \times 10^{-1}$
$10^{-4}$	$2.36 \times 10^{-3}$	$1.52 \times 10^{-2}$	$6.43 \times 10^{-2}$	$2.04 \times 10^{-1}$	$5.27 \times 10^{-1}$
$10^{-5}$	$4.93 \times 10^{-3}$	$3.17 \times 10^{-2}$	$1.34 \times 10^{-1}$	$4.25 \times 10^{-1}$	1.1

If the oxygen partial pressure at the scale–gas interface is determined by the impurity level ( $10^{-6}$  atm) in the argon gas stream, then the possibility of forming sulfide at the scale–gas interface is given by using this value of  $p_{O_2}$  in Eq. (6a). Rearranging (6a), we obtain the condition for sulfide formation at the scale–gas interface:

$$a_{Co} > (p_{O_2}/p_{SO_2})^{8/9} \cdot \exp[\frac{8}{9}(\Delta G_3^0 - \Delta G_1^0)/RT]$$

i.e.,

$$a_{Co} > (p_{O_2}/p_{SO_2})^{8/9} \cdot \exp(21,316/T + 1.139)$$

Since  $a_{Co}$  cannot exceed unity, the limiting condition becomes

$$\exp(21,316/T + 1.139) < (p_{SO_2}/p_{O_2})^{8/9} \quad (8)$$

which defines a temperature, for any given  $p_{SO_2}$  and  $p_{O_2}$  values, below which sulfide formation cannot occur.

For the present conditions, putting  $p_{SO_2} \sim 10^{-1}$  atm and  $p_{O_2} \sim 10^{-6}$  atm, the limiting temperature is about 2300°K, i.e., well beyond the range of the present investigation and beyond the limits to which the data could be extrapolated.

Thus, if equilibrium with the gas phase is established at the scale–gas interface, duplex formation is not expected to occur at that site under the conditions investigated. Now that the conditions for duplex formation have been defined, the following kinetic and metallographic features need explanation: (a) linear reaction rate period followed by a parabolic reaction rate period; (b) a sulfide layer beneath the sulfide–oxide duplex layer; (c) duplex fineness increasing with decreasing temperature.

The sensitivity of the initial linear period to the gas flow rate observed at constant temperature suggests that the reaction rate during this period is controlled by diffusion of  $SO_2$  molecules through the boundary layer formed at the scale–gas interface. The change in reaction rate is due to the change in the thickness of the boundary layer as the flow rate is varied. Under such conditions, the metal activity at the scale–gas interface remains very high during the initial period of the reaction when a duplex scale is formed.

After an initial linear period the reaction rate slows down, apparently according to a parabolic law, at all the temperatures investigated. Metallographic examination shows that during this stage of the reaction also the scale consists of a duplex oxide and sulfide structure at all the temperatures. Thus the scale–gas interface must be closer to equilibrium with the metal than with the gas, eliminating the possibility that cation diffusion through the scale is the rate-controlling step. Since the duplex structure continues to form at the scale–gas interface, uniformly over the surface, sides, and edges of the specimens and since marked scale–metal separation is not observed,



the observed decrease in the reaction rate is unlikely to be due to scale-metal separation as in the case of iron.<sup>11</sup> It is more likely to be due to a reduction in the rate of the surface reaction



as the concentrations of vacancies and electron holes increase at the scale-gas interface, due to reduction of the metal activity there as the scale thickness increases under constant rate conditions. A similar controlling step has been proposed for nickel<sup>12</sup> in these atmospheres.

The following sequence of reaction is suggested. Initially a thin oxide layer forms on the specimen surface, establishing a steep metal activity gradient, and consequently sulfide does not form at the scale-gas interface. However, sulfur dioxide penetrates the preformed oxide layer, and at sites of suitable metal activity, defined by Eq. (7), sulfide formation occurs. Initially, a thin sulfide layer forms at the metal-scale interface; eventually, however, sulfide forms within the oxide scale and from this condition in the very initial stages the usual duplex layer develops. With the inclusion of sulfides in the oxide the high ionic conductivity leads to further sulfide formation within the oxide. In time the metal activity gradient becomes shallower, increasing the width of the duplex zone.

Once the metal activity reaches the required value for duplex formation at the scale-gas interface, the duplex structure starts forming and thickens with time.

To test this hypothesis experiments were carried out with preformed oxide scales. Specimens were exposed to argon only, to allow a dense adherent oxide scale to form slowly, the thickness being controlled by exposure time. After the required thickness was reached, SO<sub>2</sub> was admitted to the atmosphere without intermediate cooling of the specimen. The resulting reaction was interrupted after suitable time intervals and the specimens were examined metallographically in order to observe the progress of sulfide formation within the oxide scale. The results are shown in Fig. 7 and indicate that thin oxide scales are penetrated very easily by sulfur. With thicker oxide scales the process is slower; however, sulfide particles have been observed embedded in the oxide layer quite soon after admittance of SO<sub>2</sub>. These results support the mechanism proposed.

In general the structure of the duplex scales formed at low temperatures is finer than that formed at high temperatures. Since the specimens are heated in the reaction atmosphere, scales formed at 840°C spend a substantial period at the lower temperature during heating. This results in a scale structure as shown in Fig. 5 with an inner layer of fine structure surmounted by an outer layer of coarser structure. This was substantiated by varying the thicknesses of the two layers by varying the times spent at the

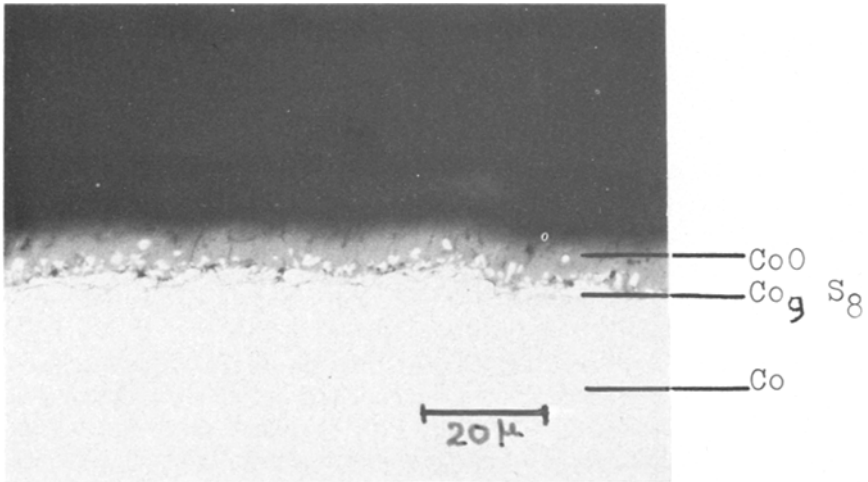


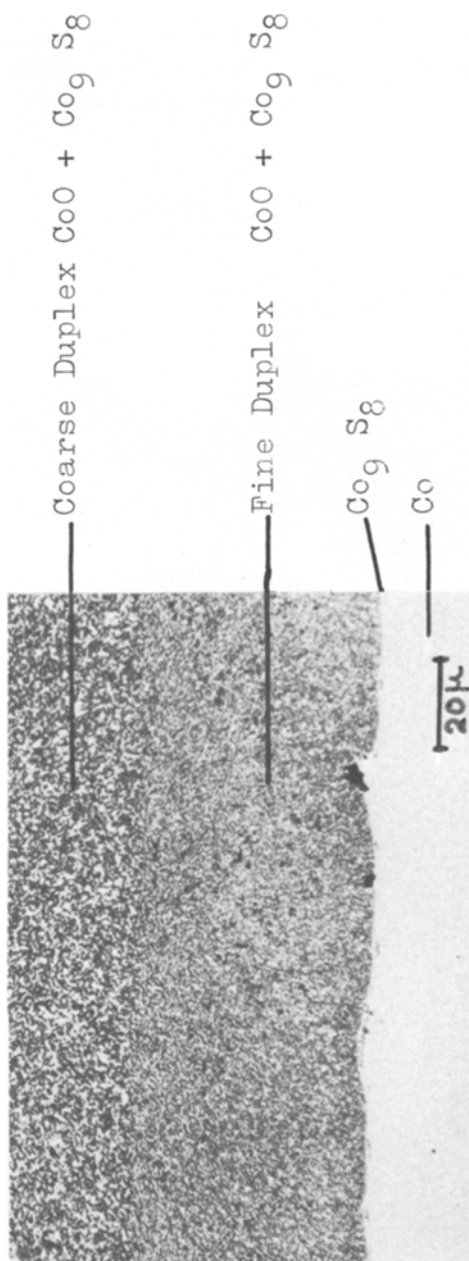
Fig. 7. 180 min oxidation, followed by 60 min in Ar-2%SO<sub>2</sub>.

lower temperature, as shown in Fig. 8. The existence of this structure sequence further substantiates that the scale grows predominantly by cation migration, with scale formation occurring at the scale-gas interface.

At temperatures above the eutectic point the same sequence of events leads to severe grain boundary penetration typical of eutectic formation between metal and sulfide. Above the eutectic point (873°C) Co<sub>4</sub>S<sub>3</sub> is the stable sulfide. X-ray diffraction examination indicates the presence of Co<sub>9</sub>S<sub>8</sub>, however. This is presumably due to decomposition of Co<sub>4</sub>S<sub>3</sub> to Co<sub>9</sub>S<sub>8</sub> and cobalt on cooling.

## CONCLUSIONS

The reaction of cobalt with atmospheres containing sulfur dioxide results in a complex scale consisting of a thin sulfide layer at the metal-scale interface followed by a thick duplex (sulfide-oxide) layer, very similar to scales as observed on nickel and iron exposed to similar conditions. The rate of the initial stage of the reaction is controlled by diffusion in the gas phase; eventually, however the rate is thought to be controlled by the incorporation of oxygen in the scale at the scale-gas interface. Thin preformed oxide layers are found to be more or less easily penetrated by sulfur dioxide as predicted from a thermodynamic assessment of the situation.



**Fig. 8.** 30 min at 780°C, followed by 60 min at 840°C in Ar-2%SO<sub>2</sub>.

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