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High temperature corrosion studies

- A. Iron - based superalloy in SO_2/O_2 atmospheres
- B. Gas - solid reaction with formation of volatile species

by

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PhD

Thesis submitted to Iowa State University

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High temperature corrosion studies

- A. Iron - based superalloy in SO_2/O_2 atmospheres
- B. Gas - solid reaction with formation of volatile species

Tai-Kang Liu

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From the Department of Chemical Engineering
Iowa State University

The thermogravimetric method for the study of high temperature corrosion under SO_2/O_2 atmosphere has been applied to Armco 18SR alloys that have different heat treatment histories, Armco T310 and pure chromium between 750 and 1100°C. The weight gain of the alloy samples follows the parabolic rate law. The volatilization of the protective Cr_2O_3 layer via formation of CrO_3 was taken into account above 900°C for long time runs. The parabolic rate and the volatilization rate, derived from fitting the experimental data to the modified Tedmon's non-linear model, were correlated using the Arrhenius equation. The activation energy of the volatilization rate constant is within the range of Lewis' study (1). The activation energy of the parabolic rate constant for pure Cr is in good agreement with the study of Hagel (2) where pure oxygen was used as the only corrosive gas. Armco 18SR-C has the best corrosion resistance of the Armco 18SR alloys. Armco T310 is not

protective at high temperatures.

The available rate data on the oxidation of chromium oxide, chlorination of chromium, oxidation-chlorination of chromium oxide, chlorination of nickel and chlorination of iron have been found to be predictable using Bartlett's model. The wide spread of temperature and pressure of the literature data for the system of oxidation of chromium oxide and chlorination of nickel enable both kinetic controlled case and the volatile product transport controlled case, which are the special case of Bartlett's model, to be predictable over a large rate range. The calculation of high temperature volatilization rate was performed using the available fluid correlation equations and the Lennard-Jones parameters derived from the molecule with similar structure and from the low temperature viscosity measurement. The lower predicted volatilization rate than the experimental rate in the literature is due to the use of the Chapman-Enskog equation with the Lennard-Jones parameters mostly derived from the low temperature viscosity measurement. This has been substantiated by comparing the reliable high temperature diffusion rate in the literature with the above mentioned calculational method, and criticizing the literature results of gas-solid reaction with volatilization of product. The experimental volatilization rates of this study are compared with the other related

studies and the mass transfer predictions. The results also substantiate the above mentioned phenomena.

1. Lewis, H. 1971. The kinetics of the oxidation process in nickel-chromium-base alloys. Metallurgia 83: 3-8.
2. Hagel, W. C. 1963. Factors controlling the high temperature oxidation of chromium. Trans. ASM 56: 583-599.

I. INTRODUCTION

Increasing the efficiency of thermal electric power plants while maintaining an economically viable condition requires using the highest possible temperature and cheapest possible fuel. Operating at temperatures above the present limit in the presence of high sulfur activity gives rise to the problem of high temperature hot corrosion of materials. The design of gas turbines, jet engines, coal gasification facilities and other high temperature equipment for service beyond present operating temperature limits is severely limited by materials availability. One typical example is the design of aircraft gas turbine material in which the hot corrosion resistance of the material was greatly reduced when mechanically stronger materials were developed by reducing the chromium content of the alloy (73).

Although the definition of hot corrosion is not unique, the following is the most generally accepted version (177): Hot corrosion is a form of accelerated oxidation which affects alloys exposed to high temperature combustion gas containing a small amount of certain impurities. However, it is generally recognized that sulfur or a sulfur-bearing compound, either in the gas mixture or deposited on the surface of the metal, is the main reason for the deterioration of the alloy by hot corrosion attack. It has been reported (100) that the measured parabolic rate

constants in $\text{SO}_2\text{-O}_2\text{-SO}_3$ atmospheres are a factor of $10^5\text{-}10^6$ greater than those observed in the pure oxidation of nickel.

Many investigators have been concerned with hot corrosion studies, but there has been a lack of unanimity of opinion as to the details of the hot corrosion mechanism. Even the measure of the extent of hot corrosion is defined differently (73,164). In general the hot corrosion phenomena is difficult to analyze due to a number of reasons. First, although it is recognized that sulfide formation beneath the product layer is the reason for further attack, there is little quantitative evidence of how sulfur or sulfur bearing compounds are transported through the outer product layer, and how this transport phenomena can be related to the observed reaction rate. Second, the chemical reactions involved in hot corrosion are numerous and complex. Different phases of oxides, sulfides and their mixtures formed during the reactions make the problem difficult to explain by thermodynamics, kinetics or transport theory alone. Third, the complexities of hot corrosion are enhanced by the many alloy variants which exist. While the available thermochemical and experimental data enable the behavior of certain alloying elements to be explained with some degree of reliability, there are clearly gaps in existing knowledge which make the prediction of alloy response most uncertain. Fourth, many experimental results are not reproducible due to

unknown reasons (164). Fifth, the formation of volatile species plays an important role in many high temperature gas-solid metallurgical reactions. This type of reaction should be considered with the scale formation reaction in order to evaluate the high temperature material performance. The oxidative volatilization of chromium oxide at very high temperatures can become significant since the latter material is one of the most important protective scales in many high temperature alloys.

The present investigation is divided into two categories which are basically related to each other in the study of gaseous corrosion of metals at high temperatures. The first is the experimental study of the corrosion behavior of several iron-based superalloys and pure chromium metals under SO_2/O_2 atmospheres between 750 and 1100°C by the thermogravimetric method. Different kinetic models were employed to analyze the data in order to get the most reliable reaction rate constants. The effects of sulfur activity and gas flow on the corrosion rate were studied. The activation energies were obtained from fitting the reaction rate to the Arrhenius equation. The reaction products were examined by metallographic procedure, X-ray diffraction method and electron microprobe analysis. The second part of this investigation reevaluated the published kinetic data of several gas-solid reactions with the

formation of volatile products with the predicted values using Bartlett's model (11). The calculation of high temperature transport properties was made by using the Chapman-Enskog equation with Lennard-Jones parameters derived either from viscosity measurements or from an element with a similar structure. The mass transfer rates in natural convection and forced convection conditions were calculated from the dimensionless correlation formula or from the heat and mass transfer analogy equation available in the literature. The derived volatilization rate of the alloys in the first part of this investigation are compared with the available literature values and with the prediction from the high temperature mass transfer calculations. The concept of calculating the high temperature gaseous diffusion coefficient is used to evaluate the results of the model predictions and the experimental results obtained either from the literature or from the present investigation.

II. LITERATURE REVIEW

A. Thermochemistry of Corrosion in Mixed Sulfidizing-Oxidizing Atmospheres

A metal in a reactive gas mixture is a complex chemical system where many different types of reactions may occur. The study of the oxidation of refractory metals by thermochemical approach has been done by Gulbransen (54,55) and Jansson and Gulbransen (75). The more complex system, in which both oxidation and sulfidation reactions take place when gas reacts with metal or alloys, has been studied thermochemically by Pettit et al. (133), Gulbransen and Jansson (58), Birks (19,21) and Quets and Drescher (135). The general agreement among the studies on sulfidizing-oxidizing atmospheres includes:

(1) A second oxide can be formed beneath the oxide layer if its activity in the gas phase exceeds that required for the reaction with the metal and if it can penetrate through the outer oxide scale.

(2) Both thermodynamics and kinetics are required in order to allow a more accurate assessment of the scale morphology and the reaction mechanism.

(3) Although the factors considered to be important with pure metals apply equally to alloys, the additional factor, such as the formation of a ternary compound and the

extent of the interaction between compounds etc., will make the thermochemical analysis of the alloy more difficult.

The sample alloys in the present investigation are commercial alloys containing Fe-Cr (Armco 18SR-A) or Fe-Cr-Ni (T310). The phase diagram of the pure component has been reviewed by Gulbransen and Jansson (58) in which the stable condensed phase under different oxygen and sulfur activities was indicated. No attempt has been made to review all of the thermochemical data relevant to the sulfidation-oxidation of metals. However, it is noteworthy that the JANAF tables (74) and other references (93,166) will give the basic data for constructing the phase diagrams.

It is well-recognized that thermodynamics may enable the prediction of the equilibrium products which might be expected to form under different conditions. However, the kinetics of reactions may be overriding in some cases, such as in a gas turbine where the residence time in the combustion system may be only a few milliseconds (134). In such cases, a prediction from thermodynamic equilibrium may be misleading. Recent studies by Rahmel (139,141,142) indicate the possibility of simultaneous formation of oxide and sulfide when the bulk gas potential only favors the formation of either oxide or sulfide. Different conditions, including the kinetic conditions of interest, have been clearly elucidated in Rahmel's studies in order to explain

the occurrence of the simultaneous formation of oxide and sulfide phases.

B. Mechanism of Sulfur Transport through the Scale

The formation of sulfide at the scale/metal interface during the scaling of an alloy under sulfidizing-oxidizing atmospheres is well-documented in the literature. This fact has led to the conclusion that sulfur can penetrate the growing oxide layer. However, according to a recent review (21), the real mechanism of how sulfur transports through the scale is still in doubt. Two possible mechanisms proposed by Birks (21) are:

- (1) Solution and the lattice diffusion.
- (2) Transport of gas molecules via physical defects.

The first mechanism requires that sulfur be soluble in the oxide. This has been used by several investigators (22,92,204) to explain the enhanced corrosion rate through the dissolution of sulfur in the oxide that resulted in an increased cation migration rate. Although the solubility of sulfur in oxide appears to be of the order of 0.01%, the mechanism is still not clear and no solution model has evolved (21).

The second mechanism has been supported by many studies. Tuck (181) has reviewed the possible mechanism for the transport of sulfur through the oxide scales. The inward

movement of gaseous mixtures containing SO_2 through small pores that are being continuously formed and healed appears to be the most likely mechanism. Similar statements about the sulfur transport through the scale can be found from different reaction systems. These include the studies of Mrowec (106,108), Hocking and Vasantasree (68), Luthra (99), Luthra and Worrell (100) and Stark et al. (169).

In addition to these investigations, several recent review papers (85,138,176) and studies (16,136,167,174) indicate that the short-circuit diffusion process, such as diffusion along pores, grain boundaries, and dislocations, are operative to some extent in the pure oxidation process. In pure oxidation, the volume/lattice diffusion will in general predominate at high temperatures while the grain boundary and short-circuit diffusion become increasingly important with decreasing temperature. For sulfidation-oxidation reactions, ionic diffusion and gaseous transport via physical defects might be the parallel mechanisms for sulfur transport through the scale (21). Which one will predominate depends on the reaction system and the operating conditions. Birks (21) suggests that more fundamental investigations be continued on the dissolution of sulfur in the oxide and the dissolution of oxygen in the sulfide under different conditions.

C. Sulfidation-Oxidation of Ni, Co, Cu and Ni-Cr Alloy

Many studies have been concerned with the corrosion kinetics of metals and alloys under mixed sulfidizing-oxidizing atmospheres. A recent review (20) indicates that increased oxidation rates are usually accompanied by the formation of sulfides in the growing scale. For pure metals, the fundamental studies on sulfidation-oxidation of Cu, Co, Fe and Ni have been carried out. For binary alloys, Fe-Cr and Ni-Cr alloys are among those of particular interest. The literature studies, excluding the Fe and Fe-Cr cases which will be discussed later, will be reviewed in this section.

1. Sulfidation-oxidation of Ni

Because of the importance of Ni in industrial application (Stainless steels, Inconels, etc.), extensive studies (1,7,9,40,43,61,72,89,92,99,100,126,153,169,204) on the corrosion of Ni in mixed sulfidizing-oxidizing atmospheres have been carried out. Due to different gas compositions and operating temperatures, the literature results are not easy to compare with each other. However, the following points are in agreement among most of the studies.

(1) The phases formed during the reaction are Ni_3S_2 and NiO with Ni_3S_2 always beneath the outer oxide layer. However, one (169) of the recent works found an exception in

that no sulfide phase was formed at the Ni-NiO interface.

(2) The reproducibility of the experimental results are usually not as good for SO_2 and Ar atmospheres. This is probably due to the small amount of O_2 in Ar gas which can significantly change the sulfur potential in the gas mixtures.

(3) Sulfur or sulfur-bearing gases always play an important role in the overall reaction kinetics. The product morphology and reaction rate strongly depend on the sulfur activity in the gas phase.

(4) No effect of gas flow rate on the reaction rate has been observed.

(5) There is general agreement that the diffusion of Ni in the Ni_3S_2 phase is much faster than in the NiO phase.

(6) In an SO_2/O_2 atmosphere, the sulfur activity is greatly influenced by the platinum catalyst which in turn influences the equilibrium gas composition.

(7) Since a low melting eutectic (Ni-Ni $_3\text{S}_2$) melts at 637°C, the very high reaction rates observed above this temperature are usually associated with the formation of liquid phases which provide rapid paths for the transport of ions.

There are several investigations where the proposed reaction mechanisms are quite different. Alcock et al. (1) used an $\text{SO}_2\text{-O}_2\text{-SO}_3$ gas mixture to study the hot corrosion of

nickel in the temperature range 500 - 700°C. They proposed a mechanism for sulfide formation by the following reaction which takes place just below the surface of the scale.

This mechanism was also suggested by Hocking and Vasantasree (68) for temperatures below 900°C when NiSO_4 was considered as a thermodynamically-stable condensed phase. However, a recent study by Luthra (99) and Luthra and Worrell (100) pointed out several conditions which would make the formation of Ni_3S_2 from NiSO_4 impossible. The chemical analysis found that the observed O : S atomic ratio was 20 : 1 which was different from the expected 4 : 1 if the above mechanism was true (99). Alternatively, Luthra (99) proposed the following reaction to explain the reaction mechanism:

As the sulfide is formed, the oxygen potential increases locally, and the sulfide formed is covered with oxide. Luthra's idea is shared by Hocking and Vasantasree (68) who believed that equation (2) is valid under conditions where NiSO_4 is not thermodynamically stable. But Luthra (99) proposed this mechanism at 603°C while Hocking and Vasantasree (68) believed it valid only above 700°C.

Luthra (99) also determined the effect of the equilibrium gas composition on the reaction rate. P_{SO_3} was found to always decrease the rate while P_{SO_2} slightly increased the rate and P_{O_2} has no effect on the reaction rate. However, Viswanathan and Spengler (185) studied the hot corrosion of the Ni-15Cr alloy and found that in the presence of O_2 , SO_3 does not contribute to the sulfidation attack of the base metal. Metallographically, Alcock et al. (1) found Ni_3S_2 to be uniformly distributed in the NiO in the two-phase mixture region whereas Luthra (99) and Luthra and Worrell (100) found that sulfide occurs in the form of isolated lumps connected by thin stringers in that region.

Wootton and Birks (204) studied the hot corrosion of Ni in the temperature range of 475-900°C by using an SO_2 and Ar gas mixture. They found no single rate law to describe the hot corrosion and the rate settled down to a constant rate of attack after an initial period. The constant rate showed that the reaction at the scale-gas interface boundary is rate determining:

This mechanism was confirmed by Luthra (99) and Luthra and Worrell (100) through analysis of the S/O weight ratio in the scale. Wootton and Birks (204) also reported that NiO dissolved about 5% S. However, there is no evidence in the

literature to support such a high solubility of sulfur in NiO (99). Therefore it is inappropriate to explain the very high reaction rate relative to that found in the $\text{SO}_2/\text{O}_2/\text{SO}_3$ mixture with the ionic diffusion theory alone. Luthra (99) believed that inward diffusion of SO_2 through NiO pores during the initial period is the main reason for inner sulfide formation. The high reaction rate observed in the SO_2 and Ar mixture is due to formation of a uniformly distributed and interconnected sulfide phase. This phase provides a rapid diffusion path for Ni ion as compared with the isolated lumps of sulfides connected by thin stringers formed in $\text{SO}_2/\text{O}_2/\text{SO}_3$ mixtures. The detailed calculation performed by Luthra (99) supported this explanation.

2. Sulfidation-oxidation of Ni-Cr alloy

Due to its wide application in corrosion-resistant equipment, many investigators (20,40,61,68,98,133,165,169, 172,182,185,205) have studied the sulfidation-oxidation of Ni-Cr alloys. In general the analysis of hot corrosion behavior in Ni-Cr binary alloys is much more complicated than with pure Ni. Lewis and Whittle (98) used an SO_2 -Ar gas mixture to study the corrosion of Ni-Cr alloy between 600 and 900°C. Weight gain vs. time curve for the different composition of alloys indicates no simple parabolic kinetics. Wootton and Birks (205) found a similar complex kinetics

curve with an SO_2 -Ar gas mixture at temperatures between 500 and 790°C. They believed that, for a low (<5%) Cr level, the formation of Cr_2O_3 may lower the Cr activity at the metal-scale interface to a value too low to support the formation of CrS initially. Eventually the Cr activity at the metal-scale interface reaches a value such that the following reaction occurs.

This displacement reaction will begin earlier as the chromium content of the alloy increases. At higher Cr content (10-20%), the initial protection followed by a rapid reaction is due to the penetration of sulfur through the initial Cr_2O_3 layer. The failure to form a protective scale below 800°C is ascribed to

(1) Formation of Ni_3S_2 by sulfur dissolution and penetration through the Cr_2O_3 layer.

(2) Rapid scale growth due to nickel ion diffusion.

Vassantasree and Hocking (68,182) used an SO_2 - O_2 - SO_3 equilibrium gas mixture to study the hot corrosion of Ni-Cr alloy between 600 and 1000°C. Weight gain data indicates that the reaction can sometimes conform to both parabolic and linear patterns and the corrosion rate can change more than once during the reaction. Four different mechanisms were proposed for the four different alloy compositions. A lower

corrosion rate was found for the 20% Cr alloy than for either pure Cr or 50% Cr alloy at 900 and 1000°C for all SO_2/O_2 ratios.

Viswanathan and Spengler (185) used different sulfur bearing gas to study the corrosion of 85Ni-15Cr alloy at 1600°F. Corrosion in 0.2% SO_2 (bal. N_2) was found to be more severe than in pure SO_2 . This is attributed to the formation of an insufficient amount of Cr_2O_3 initially to protect the base metal. Severe sulfidation-oxidation of Ni-Cr alloy can occur by direct reaction of SO_2 with the base metal. Two types of diffusion mechanism are suspected of occurring at low concentrations of SO_2 : (1) rapid short circuit diffusion along preferred networks and (2) bulk diffusion. However, the evidence for this is not well-documented.

Pettit et al. (133) studied the reaction of Ni-20Cr alloy in pure SO_2 and SO_2/O_2 mixtures. The thermodynamic analysis confirmed the formation of nickel sulfide at 1200°C when the sulfur activity in pure SO_2 gas is greater than the sulfur activity required for nickel sulfide formation. However, no explanation was given for the CrS found beneath the oxide layer when the sulfur activity in the gas phase ($\text{SO}_2/\text{O}_2=0.75$) is less than that required for CrS formation. A possible explanation is that the SO_2/O_2 gas mixture might have considerably larger sulfur potential than the calculated value using the available thermochemical data (133).

A recent experimental study by Stark et al. (169) with Ni-2 1/4 Cr alloy and $\text{SO}_2/\text{O}_2/\text{Ar}$ gas mixture around 1000°C indicated that sulfur migrated too slowly through NiO to allow penetration to the metal-scale interface unless there exists short circuit paths such as pores and cracks. The sulfur can migrate to the metal where the oxygen activity is sufficiently low to allow sulfide formation. A similar conclusion also has been indicated in the previous section regarding the mechanism of sulfur transport through the scale.

3. Sulfidation-oxidation of Co

Sulfidation-oxidation of cobalt has been studied by a number of investigators (6,14,25,88,89,90,91,105,121,127). A comprehensive review on the corrosion of cobalt and cobalt alloys under complex atmospheres has been reported by Morral (105). Nizhel'skii and Vladimirova (121) found that the oxidation rate of cobalt in SO_2 atmosphere is higher than in air and CO_2 . Brynza and Rodak (25) found that the corrosion influence of SO_2 is intensified with increasing relative humidity of the atmosphere. Both investigators (25,121) found that the parabolic rate law applies. Metallographically, CoS and CoO product layers were found (6,127) when Co is reacted with SO_2 at high temperatures. CoO is on the surface and CoS is in contact with the metal.

The oxidation of Co in $O_2/CO_2/SO_2$ atmospheres between 700 to 1200°C has been studied by Konev et al. (89,90,91). The corrosion rate was found to be proportional to the SO_2 concentration. The scale was found to consist only of CoO. The absence of CoS was perhaps due to the smaller sulfur activity in $O_2/CO_2/SO_2$ atmosphere as compared with the experiments of Pannetier and Davignon (127). These investigators (89,90,91) also suggested that the dissolution of sulfur into the lattice of CoO increased the cation vacancy concentration and thus the diffusion rate.

4. Sulfidation-oxidation of Cu

Very little fundamental work has been done to study the gaseous corrosion of copper in sulfidation-oxidation atmospheres. Although the earlier studies (40,60,70,184) did not include metallographic investigation, there was agreement that the SO_2 will accelerate the reaction rate. Recent work to study the effect of SO_2 on the high temperature oxidation of Cu has been carried out by Birks and his co-worker (18,22) between 700 and 1000°C. Under all the conditions studied, the oxidation was found to follow a parabolic rate law. The effect of SO_2 on the reaction rate was found to depend on the formation of the $CuC \cdot CuSO_4$ phase. If the gas composition approaches that in equilibrium with $CuC \cdot CuSO_4$, the reaction rate is proportional to the SO_2 pressure. However, if the

gas composition is far removed from those in equilibrium with $\text{CuO} \cdot \text{CuSO}_4$, SO_2 has little effect on the reaction rate. Very large increases in the corrosion rate were observed when the gas composition was in the range where the $\text{CuO} \cdot \text{CuSO}_4$ phase was stable. The oxides formed were Cu_2O and CuO . It is suggested (22) that an appreciable amount of sulfur can dissolve in both phases and this is thought to favor the formation of additional vacancies on the cation lattice, thereby producing the observed increases in the oxidation rate. Very large increases in corrosion rate were observed when the intergranular network of $\text{CuO} \cdot \text{CuSO}_4$ was present in the CuO layer. The liquid eutectic between CuO - $\text{CuO} \cdot \text{CuSO}_4$ would greatly increase the transport process in the scale and would explain the very high reaction rate associated with the presence of $\text{CuO} \cdot \text{CuSO}_4$. It is suggested (22) that the formation of an Cu_2O - Cu_2S duplex structure at the metal-oxide interphase during the reaction was formed by the inward penetration of sulfurous species through an apparently compact oxide layer.

D. Sulfidation-Oxidation of Fe

The widespread occurrence of sulfur in fuels has resulted in continuous interest in the corrosion behavior of combustion gases upon iron and its alloys. However, most of the earlier works done in this field are qualitative in

nature (40). The study by Ross et al. (152) on mild steel found the scaling rate in mixtures of N_2 and SO_2 increased with temperature and the SO_2 concentration. Hydrogen was found to accelerate the corrosion rate in the N_2/SO_2 mixture whereas oxygen was found to reduce the corrosion rate. An empirical equation related the weight gain with the temperature and SO_2 concentration has been given in their study. However, no metallographic details and reaction mechanism studies were found. The earlier work indicated three eutectics existed in the Fe-S-O system (42): Fe-FeS-FeO at $925^\circ C$, FeS-FeO at $940^\circ C$ and Fe-FeS at $988^\circ C$.

Rahmel and his coworker (137,139,140,141,142,143,144) between 1969 and 1975 have conducted a systematic investigation of the corrosion of iron in sulfidizing-oxidizing atmospheres. A comprehensive survey has also been prepared by Birks (17).

Rahmel (137,143) studied the scaling of iron in CO/CO_2 mixtures with small addition of SO_2 and H_2S between 700 and $900^\circ C$. A linear rate law was obtained when the SO_2 content was less than 1.0 %. A changeover to a parabolic rate law occurred after a short period when greater concentration of SO_2 was used. The linear rate was explained by the sulfur compound diffusion through the gaseous film layer as the rate controlling step for the following reasons:

(1) There was always a linear relationship between the linear rate law constant and the concentration of sulfur compound in the gas.

(2) When the amount of H_2S or SO_2 added was small, the scale formed near the incoming gas stream was thicker than that formed at the other end.

(3) The linear rate constant was proportional to $1/2$ power of the flow rate and was not influenced by the temperature change.

(4) Experiment with Ar/SO_2 gas mixture gave a similar weight gain vs. time curve as the $CO/CC_2/SO_2$ mixtures. The linear rate constant of the two cases is shown in Figure 1. The 20% higher rate in Ar is due to the lower kinematic viscosity of Ar than of the CO/CC_2 mixture, which is understandable when the gas phase transport of the sulfur compound is the rate determining step.

Metallographic study (144) of iron sulfidation-oxidation reactions also has been performed between 700 and 900°C by adding small amount of sulfur-bearing gases in CO/CO_2 mixtures. The formation of FeO in COS -containing gas when only FeS is the thermodynamically stable product was explained to be due to the diffusion of the iron ion through the scale which was faster than either the phase reaction at scale/gas interface, or the supply of the sulfur bearing compound transported through the gaseous film layer to the

Figure 1. Linear rate constant for pure iron as a function of SO_2 concentration in Ar and 80% CO +20% CO_2 (from Kahnel, 1969).

scale surface. In this case, the scale surface is not in equilibrium with the gas phase. As soon as the diffusion in the scale becomes the slowest step and equilibrium is attained between the scale surface and the gas phase, only the thermodynamically stable phase of FeS will be formed.

Recent studies on the corrosion of iron in sulfur and oxygen containing gases have been conducted by Rahmel (140) with $\text{SO}_2/\text{O}_2/\text{N}_2$ gas mixture at 900°C , and by Flatley and Birks (42) with SO_2/Ar mixture between 500 and 900°C . Both studies agree that the initial constant reaction rate is controlled by the diffusion of SO_2 through the gaseous film layer to the scale surface. Under all conditions studied, Rahmel (140) believed that cation diffusion will become rate determining and true parabolic kinetics will be observed. However, Flatley and Birks (42) found that the initial parabolic rate was due to scale-metal separation at sample corners, and not due to cation diffusion control as proposed by Rahmel (140). Eventually true diffusion controlled kinetics are imposed when sulfide stops forming and an outer layer of oxide forms without any sulfide inclusion. The thermodynamic analysis by Flatley and Birks (42) indicates the impossibility of iron sulfide formation without iron oxide formation. A complete layer of FeS is not expected to form. This is due to the fact that the formation of FeO will lower the local oxygen partial pressure and increase the local sulfur pressure so

that FeS and FeO will form together to produce an intimately mixed lamellar structure (42). Their explanation was in agreement with the earlier investigation by Foss (151) who studied the corrosion of mild steel by SO₂ gas. Although Ross (151) proposed that the SO₂ transport process is the rate controlling step in the earlier reaction step, no metallographic details were available to substantiate the claim. This claim has been proven by Flatley and Birks (42) and later by Rahmel (140) by chemical analyses which give a sulfide/oxide molar ratio about 1:2, which is just equal to the stoichiometric ratio of S/O in SO₂ molecules.

Rahmel (139,141,142) made an analysis of the rate controlling step in the oxidation-sulfidation of iron based on his previous studies. The kinetic conditions for simultaneous formation of oxide and sulfide in reactions of iron with gases containing sulfur and oxygen bearing compounds were discussed. Since most of the investigators in this field did not include the determination of the reaction kinetics and the rate controlling process, Rahmel's theory (141,142) cannot be checked against the results reported in the literature. The major conclusions of his papers are:

(1) If the rate controlling step is the reaction at the Fe/FeX phase boundary or the diffusion process in FeX where X is the oxidant, the addition of a second oxidant has no effect on the reaction rate and only the thermodynamically

stable phase will be formed.

(2) If the rate controlling step is the reaction at the scale/gas phase boundary or the transport process through the gaseous film layer, the addition of a second oxidant will increase the reaction rate. Both FeO and FeS will be formed simultaneously in this case whenever oxygen or sulfur is the second oxidant.

This idea, which basically is in accord with Flatley and Birks' (42) analysis, separates the kinetic condition from the thermodynamic consideration and could possibly be applied to other metal-two oxidant systems. However, at the present time, only the case for iron has been investigated (142).

E. Sulfidation-Oxidation of Fe-Cr Alloy and Superalloys

Although there are many studies on the sulfidation of Fe-Cr alloy (7,40,107,109,111,114,115,173,207) or the oxidation of Fe-Cr alloy (9,29,30,41,69,96,163,180,199,200,201,202,203), the combined effect of sulfidation-oxidation gas on this kind of alloys has yet to be thoroughly investigated. A recent review by Birks (20) gave only one reference paper (154) about this topic. A computer literature search of Chemical Abstracts from 1970 to 1978 also gave only limited papers (18,20,118,154,155,159,168) in this field. A review (12) that covered more than 1500 references on the corrosion and deposits from combustion gas has been

prepared by Battelle Memorial Institute in 1970. However, most of the references covered are salt-induced hot corrosion studies which are not of interest to this work. Hancock's critical review (62) covered several earlier studies (120,161,178) done before 1970. Due to the complexity of the problem, most studies have been confined to the qualitative approach. The more fundamental analysis of the reaction, even up to the present time, is still almost unknown (20,142).

In general the kinetics of the earlier studies (40,120,161,178) were not assessed in detail and no microstructure studies were made. However, a number of generalizations can be derived from the earlier studies:

(1) Low chromium alloys would be subject to rapidly increasing deterioration with increasing temperature. High chromium alloys generally are more resistant to corrosion than the low chromium alloys, especially if the sulfur concentration in the gas atmosphere is high.

(2) Reducing atmospheres are generally more aggressive than oxidizing ones, requiring higher chromium levels for protection with the same nickel content in Fe-Ni-Cr alloys.

(3) The rate of attack of the steel was largely independent of the gas composition when using SO_2 and O_2 gas mixtures (120,178).

Recently, Spengler et al. (168) compared the sulfidation-oxidation corrosion behavior of superalloys in laboratory tests with the long-time service exposed superalloys. The samples consisting of a variety of alloys were exposed to identical long-time field service conditions as well as subjecting specimens of the same alloy to various laboratory test. The experimental results indicated that the composition, thickness, and complexity of the scales and the affected alloy region (AAR) vary with many factors such as the specific alloy composition, test conditions, test time, type of test and location of the individual specimen. They found a completely changed microstructure on the outer portion of the AAR with respect to the base structure and the most significant change in the AAR was the lower Cr concentration as compared with the base alloy. They also found that the Cr level of the AAR appeared to be dependent on the protectiveness of the oxide scale. The width of the AAR increased with time. The Cr concentration at the AAR/scale interface drops rapidly during first few hours of corrosion, but decreases after the initial drop at a reduced rate. One of their distinct conclusions is that the weight loss measurements cannot be used to measure corrosion, since these values reflect only the amount of scale formed but do not take into consideration the extent and microstructure of AAR (168).

Salisbury and Birks (154) studied the corrosion of the iron-chromium alloy at 800 and 992°C in an atmosphere of argon containing 2.5% SO₂. The effect of Cr was shown to decrease the parabolic rate constant. With an alloy containing 10% Cr and more, the oxidation was completely passive up to 24 hours. The rate constants in SO₂-Ar atmosphere are higher than in pure oxygen, although this effect is reduced as the Cr content of the alloy is increased. The parabolic rate constant of oxidation of 10% Cr in 2.5% SO₂-Ar mixture at 800°C is found to be $3.11 \times 10^{-9}/\text{gm}^2\text{-sec}$, which is approximately 2 times greater than that in pure oxygen. In addition, their experimental data gave 8.7 times the parabolic rate constant of oxidation in pure oxygen when the Cr content of the alloy was decreased to 3%. Kinetic studies by Salisbury and Birks (154) revealed that alloys containing 5% Cr and above show the same order of reaction rate which has been observed in pure oxygen. No initial linear rate law was observed for that range of alloy composition. However, this phenomena might not be true for other gas compositions since no work on the effect of gas composition on the oxidation rate has been done. For low Cr alloys, the enhanced corrosion rate is due to the rapid transport of iron ions through the iron sulfide networks.

Thermodynamic analysis by Salisbury and Birks in the same study (154) indicates that the formation of chromium

oxide is more favored than the formation of iron oxide, although the partial pressure of oxygen in the atmospheres is high enough to support the formation of both. As the oxides formed, the local oxygen partial pressure is reduced thus providing conditions suitable for sulfide formation. Under no circumstances in their investigation will the oxide layer become completely resistant to SO_2 penetration. This is consistent with the results of other studies (21,118,128). Although Salisbury and Birks (154) did little metallographic study on the high chromium alloy (>10%), they arrived at the conclusion that the behavior of iron-chromium alloys in SO_2 -Ar atmosphere can be explained by a combination of the features shown by iron-chromium alloys in oxygen and pure iron in SO_2 -Ar atmospheres.

The corrosion behavior of material for coal-gasification applications has recently been studied extensively. The corrosive gases in the coal gasification environments are characterized by their high sulfur activities. Natesan and Chopra (118) investigated the corrosion behavior by simulatively exposing 3 different kinds of commercial alloys to 5 different complex gas environments derived from 5 different coal gasification processes. The thermochemical analysis reveals that increasing the Cr content of the alloy enlarges the stability region of chromium oxide. They (118) also found that chromium sulfide formation in the subscale is

unavoidable. Another important result of their thermochemical analysis is that the nickel content of the alloy will limit its performance due to the formation of liquid nickel sulfide which can lead to an enhanced corrosion rate at a temperature between 1000 and 1400°K. For this reason, eliminating or minimizing the use of nickel is one of the goals in designing coal-gasification service alloys in the latter investigation (128). The experimental work involves exposing 4 kinds of commercial alloys to 3 different kinds of gas environment with fixed sulfur activity but different oxygen and carbon activity for 136 hours. The thermochemical diagram combined with the scanning electron microscope photographs appears to satisfactorily explain the experimental result. The fundamental process related to the coal-gasification process, such as oxidation, sulfidation, carburization etc. has also been discussed in another study (116).

Recently, a comprehensive program to design the sulfidation-resistant alloy for coal gasification service has been instituted by Perkins and Bhat (128,129,130,131). It has been found that the addition of 2% Al to an 18% Cr alloy produced a compact oxide scale which provides a much better barrier to sulfidation. The oxide formed is still chrome based and is very adherent. With the addition of 3% or more Al to 18-20%Cr alloys, compact scales of alpha-alumina are

formed at 1800°F gasification atmospheres. Alpha-alumina compact scales are excellent barriers to sulfidation. Since the sulfur potential in coal gasification environment (app. 10^{-6} atmosphere) is much greater than in SO_2/O_2 mixture ($<10^{-20}$ atmosphere at 1000°C), any alloy that is resistant to corrosion in the former environment will probably survive in the latter atmosphere. They found that 12-18% Cr and 4-10% Al had good potential for design of an improved sulfidation resistant alloy (128). However, a minimum of 18% Cr appeared to be required for long-term service (129).

III. EXPERIMENTAL

A. Materials

The samples supplied by Armco Steel Corporation Research Laboratory were the alloys Armco 18SR and T310. The samples were 0.05 inch x 1 inch x 2 inch in size. A hole was punched at one end of the plate sample prior to the heat treatment by the Armco Steel Corporation. The details of the heat treatment and the appearance of sample before testing is given in Table 1. The chemical analysis of the sample, as reported by the supplier, is given in Table 2. These samples do not need any pretreatment before corrosion testing. In addition to the Armco 18SR and T310, high purity chromium samples with the same dimension as the superalloys were also run at high temperatures under an SO_2/C_2 atmosphere. The chromium ingot was obtained from the Materials Research Laboratory and has a purity of 99.96%. The chromium samples were cut from the ingot. After a suspension hole was drilled in each, these were wet ground through 320 and 600 silicon carbide paper and cleaned with acetone. The samples were weighed using a precision balance. The surface area was calculated from the micrometer measurements.

Table 1. Heat treatment history of the sample alloy.

Sample	Heat treatment
18SR-A	Cold rolled + annealed in air + glass blasted (silvergray).
18SR-B	Cold rolled + cleaned + heated in air at 1 °C/min. to 1000 °C + held for 16 hours + air cooled (gray).
18SR-C	Cold rolled + cleaned + heated in air at 1 °C/min. to 1200 °C + held for 16 hours + air cooled (dullgray).
T310	Degreased 310 (silver).

Table 2. Chemical analysis (wt.%) of the sample alloy.

Element	18SR	T310 ¹
Fe	bal.	bal.
Cr	17.720	25.00
Al	1.800	-
Si	0.690	0.40
Ti	0.330	-
Ni	0.280	20.00
Mn	0.180	1.50
C	0.034	0.25
P	0.021	-
S	0.014	-

¹As reported from reference (118).

B. Gas Metering and Mixing Equipment

The schematic representation of the gas metering and mixing equipment for this study is shown in Figure 2. The ultra high purity oxygen, supplied by Scientific Gas Products, was reported to have the following composition: O_2 (>99.97%), Ar (<50 ppm), N_2 (<100 ppm), H_2O (<2 ppm). The anhydrous SO_2 gas was supplied by Matheson Gas Products. The trace amount of water in both gases was removed by passing them through a calcium chloride and a phosphorous pentoxide tower prior to entering the reaction zone. The glass beads inside the mixing tower were used to enhance the homogeneity of the mixture. Capillary tubes with a diameter of approximately 0.4-0.7 mm were used in each of the manometers so that the individual flow rate between 0 to 7 ml/sec can be obtained. For very low flow rates, a small diameter capillary tube is preferred in order to obtain the highest sensitivity in the height differential of the liquid in the manometer. Both manometers were calibrated with nitrogen gas. The flow rate was measured using 50 ml burettes with soap bubbles as indicators. The identical flow rate obtained from the gas measuring part of the equipment and the gas carrying teflon tube before entering the heating zone eliminated any leakage possibilities.

Dibutyl-phthalate (density = 1.048 at room temperature) was used as the working fluid in the manometer as well as in

Figure 2. Schematic representation of the gas metering and mixing equipment.

the height-adjustable reservoirs. Because of the pressure drop in the gas cylinder, the flow rate will probably drop below the desired setting. The height of the adjustable reservoirs is used to monitor and control the flow rate during the long-period experiment by allowing a small amount of metered gas to bubble through it. Preliminary experiments showed that there is little interaction between the oxygen and dibutyl-phthalate. However, dibutyl-phthalate can absorb about 13% (by volume) SO_2 in a 100 hours run. Since the experimental measurement of the density of the working fluid before and after the interaction with SO_2 differs less than 0.6%, it is safe to neglect this difference within the accuracy range of the experiment. In order to overcome the effect of the small interaction between SO_2 and dibutyl-phthalate and also obtain the maximum possible accuracy, the level difference between the two arms of the manometer was used as a reference indicating the flow rate. The calibration curve is shown in Figure 3. The third gas metering arrangement of Figure 2 is the same as the other two. It is used for metering the inert gas.

C. Sample Heating and Weight Measuring Equipment

The schematic representation of the sample heating and weight measuring equipment is shown in Figure 4. The major component of the arrangement includes a Lindberg type 54442

Figure 3. Flow rate calibration curve for the manometers using dibutyl-phthalate as the working fluid.

Figure 4. Schematic representation of the sample heating and weight measuring equipment.

tube furnace, a Lindberg type 59544 - C3 control/programmer system, a Cahn RH automatic electrobalance and controller, a potentiometric Sargent recorder (model MR) and a 66 mm diameter quartz tube column reactor.

The range of sample weight change during an experiment was estimated before the run and the MASS DIAL RANGE in the balance controller was set accordingly. The desired sensitivity of the recording can be obtained by the RECORDER RANGE setting. A typical experimental run with MASS DIAL RANGE = 0.5 gm and RECORDER RANGE = 10 mg is estimated to give a sensitivity of 2.5×10^{-4} gm per line when using the Sargent recorder chart no. S-72166, provided the input range setting in the Sargent recorder is equal to 5 mv. The actual sensitivity of a typical recording is 2.469×10^{-4} gm. This was obtained from changing the weight by turning the MASS dial and counting the actual movement of the recorder pen. The noise on the recorder chart for the typical run is in the order of 10^{-5} gm peak-to-peak. After the electrobalance has been calibrated, the weight change during the experiment can be readily calculated.

The split furnace can attain a reaction temperature between 200°C and 1200°C through a programmable controller. The furnace heating zone is 25 inches long with a silicon carbon heating element packed inside. The sample was hung in the middle of the furnace inside the quartz tube with a 15

mil diameter platinum wire. The platinum wire functions both as the suspension wire and the catalyst. In addition to the platinum wire, a platinum foil was also hung above the sample to ensure that a $\text{SO}_2/\text{O}_2/\text{SO}_3$ equilibrium composition prevailed at the reaction temperature. The SO_2/O_2 gas mixture is flowing downward in the quartz column. The downward flow pattern was chosen in order to reduce the aerodynamic force on the sample suspension (26).

Since the gas mixtures are highly corrosive to the delicate electrobalance, the protection procedure used by Vasantasree and his co-workers (182,183) in similar studies was used. The design essentially involves putting a Pt-Au-Pt composite suspension wire through the capillary with a small amount of oleum seal inside. The Au-part was chosen to pass through the oleum seal due to the negligible surface tension between them. Several modifications were made to satisfy our requirements:

(1) The liquid seal used in this arrangement is the fuming H_2SO_4 with a density equal to 1.98 gm/ml at room temperature. The 4 mm diameter constriction and 3 mm depth of seal in the original design was changed to 2.5 mm diameter constriction and 6 mm depth of seal. This change prevented the hot gases from destroying the liquid seal at high temperatures.

(2) The preliminary runs showed that the oleum seal accumulates its volume during the reaction. This is due to the absorption of moisture (182). Because of the longer run (typically 100 hours at 750°C) compared with the study of Vasantasree et al. (182,183), the seal will partially drop down along the wire after the first 10 hours and every 5 to 6 hours. A small glass tube with its one end slightly in contact with the seal can overcome this drawback by letting the residual oleum falling along the tube to go to the small reservoir attached to the glassware above the quartz column.

The details of the glassware design are shown in Figure 5. The upper part of the glass equipment above the seal was connected to the electrobalance and the water suction pump. The water suction pump protects the electrobalance from the corrosive gases in the event that the oleum seal is lost. Removal of exhaust gases at the bottom of the reaction column is carried out through a loosely coupled funnel connected to a water suction pump. Any significant suction effect at that end is not allowed in order to maintain the desired hydrodynamic conditions inside the reactor. The water suction pump is open to the atmosphere so that the whole system remains at atmospheric pressure. The sample alloy is connected to the suspension wire by a platinum hook. The platinum suspension wire inside the quartz tube is connected with the lower part of the Pt-Au-Pt wire by a small platinum

Figure 5. Details of the glassware design.

hook. The hook connector simplifies the sample loading and unloading procedure before and after each experiment.

A Pt/Pt-13% Rh thermocouple was installed in the quartz column directly opposite the sample. This thermocouple, calibrated against a N.B.S. thermocouple (reference no. 2 N.B.S. test no. 190835A dated 3-7-1967) was put through an ice bath reference junction, thereby eliminating any error in temperature measurement. The output from the thermocouple was measured by a Hewlett Packard Co. model 3440A digital voltmeter. The conversion of millivolt to actual temperature was made by using the calibration table for a Pt/Pt-13%Rh thermocouple.

D. Experimental Procedure

The superalloy samples obtained from the Armco Steel Company have been specially heat-treated. The samples were not pretreated prior to the experiment. The chromium samples were polished before the experiment. The weight of the sample, the Pt-hooks, the Pt-wire and the Pt-foil catalyst were measured before and after each run using a Mettler balance capable of weighing grams to the fourth decimal point. The sample dimensions were measured with a micrometer before each run.

Since the sample was positioned before the start of the experiment, the heating to the desired temperature was

carried out under purified Ar gas to avoid any undesired reactions during the heating period. The high purity argon, supplied by Scientific Gas Product, was reported to have the following composition : Ar(>99.999%), O_2 (<2 ppm), N_2 (<6 ppm), H_2O (<3 ppm). The Ar gas was passed through a molecular sieve column to remove the residual moisture. It was then passed through titanium powder at 617°C to remove the residual oxygen. This purification process maintained the lowest possible oxygen potential during the heating-up period. It normally takes two hours to attain a reaction temperature of 750°C and about four hours to attain 1100°C. The recorder indicated a non-significant weight change during this period. While the sample is heating up, the SO_2/O_2 gas mixture at the desired composition and flow rate is channelled through a bypass. Since the alloy is highly oxidation-resistant and the experimental run is long, this method proved to be the best way to start the reaction. After the desired temperature was attained, the Ar gas flow was stopped and the SO_2/O_2 gas mixture was passed through the reaction tube. Due to the change of flow rate which might change the aerodynamic equilibrium in the system, the first five to ten minutes of the experimental data were not used. The actual weight gain during this initial period was determined by extrapolating the total weight-change curve to time zero. No high vacuum grease is used in the glass joint near the top of column in

order to avoid the difficulty of separating the glassware after cooling.

After the reaction run was completed, the main power was turned off and the gas mixture flushed with Ar gas to prevent further reaction. The sample was taken out and weighed after cooling to room temperature. Special care was taken in handling the reacted sample so that none of the solid product was lost or displaced. The glass equipment was cleaned and dried after each run. A typical experimental procedure is summarized in Table 3.

E. Examination of Solid Product

1. Optical microscope study

After completion of the kinetic measurement, a cross section of the specimen was prepared by a standard metallographic technique using Plastimet as mounting material. The samples were examined under high magnification using a Baush and Lomb Company Model Research-II microscope. Pictures with magnification of 1000X were taken using an oil immersion between the object and the microscope. The oxide phase was dark in reflected light whereas the sulfide phase was bright. Special care was taken for samples with oxide scales that spalled upon cooling.

Table 3. Typical experimental procedure.

- (1) Adjust the seal height. Put the sample in its position inside the column reactor. Adjust the reactor position so that the Au-part of Pt-Au-Pt suspension wire passes through the center of the small constriction filled with oleum seal. Put the counterweight on the balance.
- (2) Set the desired dial readings on the electrobalance. Turn on the balance controller and the recorder. Let the whole system go to steady state by running it for several hours or overnight.
- (3) Open the water suction pump. Turn on the high speed hood timer and the power for the Ar purification heating furnace for at least one hour before introducing the Ar gas into the reactor.
- (4) Let Ar gas flow slowly through the system. The flow rate must not influence the stability of the liquid seal. Get the temperature indicator (HP voltmeter) ready by making the reference temperature zero.
- (5) Set the desired temperature on the furnace controller and turn on the main power of the heating furnace. This temperature setting only serves as an approximation. The true temperature is obtained from the digital indicator conversion. Make adjustment on this setting in the final heating up period if necessary.

Table 3. (continued)

(6) Adjust the SO_2/C_2 flow rate and the desired composition through the bypass system when the reaction temperature is approached.

(7) After the desired temperature is attained, switch from Ar to SO_2/O_2 gas mixture and make a mark on the recording paper.

(8) During the run, constantly check the stability of the liquid seal. Also constantly check the individual flow rate. Adjust the reservoir height if necessary.

(9) After the experiment, the gas mixture is replaced with high purity Ar gas. Cool down the system to room temperature by turning off the main power.

(10) Turn off the water suction pump. Leave the electrobalance, controller and recorder running during the cooling period in order to detect the possibility of the scale flaking off.

(11) Remove the sample and weigh the suspension components after attaining room temperature.

2. X-ray diffraction study

The X-ray powder diffraction method was used to identify the composition of the product phase. The identification of an unknown crystalline phase was made by matching the powder pattern Bragg angle and reflected intensities of the unknown substance with those given in the powder pattern standards. This method generally constitutes an important branch of qualitative chemical analysis.

X-ray diffraction analysis was made using a Debye-Scherrer powder camera with a diameter equal to 11.459 cm. The X-ray generator was produced by North American Philips Co. Type 12045B/2. The sample for analysis was obtained from the scale that flaked off during the cooling period. After being ground into a fine powder, the sample was put into a 0.3 mm diameter capillary tube which served as the target of the incident X-ray. Copper radiation was used in this analysis. The Bragg angle of the different crystal plane was recorded on a negative film that was mounted on the inside surface of the circular powder camera. It normally took eight hours to complete one analysis.

IV. TREATMENT OF EXPERIMENTAL DATA

A. Available Models for Treatment of High Temperature Reaction Data

The extraction of high temperature corrosion rate data from thermogravimetric experimental results at times makes possible the elucidation of the corrosion mechanism. From an engineering point of view, the corrosion rate is perhaps the most important metal or alloy parameter in the corrosive gas environments. Since the solid product of the gas-metal (or alloy) corrosion reaction is usually formed on the metal surface, the reaction rate is usually measured and expressed as weight gain per unit area. Various empirical rate laws for describing the reaction rate have been developed. The most commonly used rate laws are the linear form,

$$W = K_1 t \quad (5)$$

the parabolic form

$$W^2 = K_p t + C \quad (6)$$

and the logarithmic form

$$W = K_g \log(C't + A) \quad (7)$$

where W is the weight gain per unit area, t is time, K_1 , K_p and K_g represent the rate constant for the corresponding rate

law, and C and A are constants. These equations are used under conditions where the volatilization effect of the solid product is negligible. Different mechanisms associated with each of above rate laws have been discussed in many books (44,64,94,110). In general, linear oxidation is characteristic of metals for which a porous or cracked scale is formed so that the scale does not represent a diffusion barrier between the gas and the metal. The parabolic behavior is associated with the formation of a thick, coherent scale on the metal surface. The logarithmic rate is not yet completely understood. It is generally recognized that the parabolic and logarithmic rates are the most desirable for metal or alloys applications at high temperatures under a corrosive environment. The linear rate is the least desirable, since the weight gain increases at a constant rate with time.

For many metal-oxygen or metal-halogen reactions, the solid product initially formed follows the parabolic rate law. However, when the reaction time is long or when the reaction temperature is high, deviation from parabolic to the linear rate law occurs. This is generally attributed to the volatilization of the solid product, or further reaction of the solid product with the corrosive gas to form another volatile specie, following a linear rate law. A typical example is the high temperature oxidation of alloys forming

Cr_2O_3 protective layer where parabolic kinetics occurs due to further reaction of Cr_2O_3 with oxygen to form the volatile specie CrO_3 . If the reaction temperature is not very high or the reaction time is not very long (depending on the reaction system), the volatilization kinetics is usually negligible compared with the parabolic kinetics. Many investigators (9,30,33,52,66,97,175,179,186) have studied the kinetic model of this type of reaction, or simply applied some empirical models to fit the reaction curve. Those studies (9,30,52,97,175,179) using alloys forming Cr_2O_3 protective layer are of great interest to the present investigation due to the similar selective oxidation of the chromium in the Armco 18SR alloys in this study where the reaction temperatures and the reaction times are high and long enough for the volatilization to be significant. A summary of the available model equations taking into account both the volatilization effect and the parabolic kinetics for the alloys forming Cr_2O_3 protective scale is given in Table 4.

Tedmon's model (179) was derived from the following differential equation that takes into account both the diffusive transport of ionic species with parabolic kinetics and the oxidation of Cr_2O_3 to a volatile specie with linear kinetics. Tedmon's model equation

Table 4. Kinetic models for the paralineer behavior of alloys forming Cr_2O_3 layer at high temperatures.

No.	Model equation*	Alloy system	Remark	Ref.
1	$t = \frac{K_d}{K_s^2} \left\{ -\frac{K_s}{K_d} X - \ln \left(1 - \frac{K_s}{K_d} X \right) \right\}$	Cr and Fe-Cr	Original derivation	179
2	$t = \frac{K_p/2}{\alpha^2 K_v^2} \left\{ -\frac{\alpha K_v (\Delta M/A)_0}{K_p/2} - \ln \left(1 - \frac{\alpha K_v (\Delta M/A)_0}{K_p/2} \right) \right\}$	Ni-20Cr-2ThO ₂	Separated the effect due to oxygen pickup and chromium loss	52

- * t : Time (sec).
 K_d : One half of the Tammann's rate constant (cm^2/sec).
 K_s : Proportional to K_v (cm/sec).
X : Scale thickness (cm).
 K_v : Volatilization rate constant for loss of Cr_2O_3 via CrO_3 formation ($\text{gm}/\text{cm}^2\text{-sec}$).
 K_p : Parabolic rate constant in terms of oxygen pickup; $(\Delta M/A)_0^2 = K_p t$.
 α : Weight fraction of oxygen in Cr_2O_3 .

Table 4. (continued).

No.	Model equation*	Alloy system	Remark	Ref.
3	Rate law $W^2 = K_p t$ $t_n = (X_f/K_s) \{-n - \log(1-n)\}$ Rate law $W^3 = K_c t$ $t_n = (X_f/K_s) \{-n - 0.5 \log[(1-n)/(1+n)]\}$ Rate law $W^4 = K_q t$ $t_n = (X_f/K_s) \left[-n - \frac{1}{3} \{ \sqrt{3} \tan^{-1} \right.$ $\left. - \frac{(2n+1)}{\sqrt{3}} \} + \log[(1-n) \right.$ $\left. / (n^2 + n + 1)^{1/2} \} \right] + \frac{1}{3} \{ \sqrt{3} \tan^{-1}(-1/\sqrt{3}) \}$	Dispersion Containing alloys forming Cr_2O_3 scale	Rearranged & extended Tedmon's model to other empirical rate laws	175
4	$W = K_p' t^{1/2} - K_v t$	Fe-Ni-C-30Cr	Commonly used model	30
5	$W = K_p' t^{1/2} - K_v t + C$	Ni-Cr	Commonly used model	97

* X_f : Limiting scale thickness when the rate of thickening is equal to the rate of thinning $= K_p'/2K_s$.

t_n : Time taken for the scale to grow to a thickness which is a fraction n ($0 < n < 1$) of X_f .

W : Weight gain per unit sample area (gm/cm^2 -sec).

K_p' : Square root of K_p .

$$\frac{d X}{d t} = \frac{K_d}{X} - K_s \quad (8)$$

where X is the instantaneous scale thickness, K_d is one half of Tammann's parabolic rate constant, and K_s is proportional to the volatilization rate. The integration of the above equation results in the model equation given in Table 4. This model has been modified by Giggins and Pettit (52) in order to calculate the parabolic rate constant due to the oxygen pickup reaction. Hagel's correlation (59) on the Cr_2O_3 volatilization rate was used to calculate the K_p in the work of Giggins and Pettit using the Newton-Raphson iteration method (52). However, the uncertainty limit of Hagel's correlation (59) and the time-varying behavior of the calculated parabolic constant in a single run decreased the overall accuracy of the rate estimations. Stringer (175) studied the functional form of rate curves for high temperature oxidation by using different rate laws as given in Table 4 to fit the experimental data. Since there is a lack of mechanistic interpretation of the higher order model equation, the significance of this curve fitting procedure is still in doubt. The model used by Croll and Wallwork (30) and Lewis (97) only differs in the additional constant C in Lewis' study in order to cover the non-conformity of the early part of the rate curve. The term $K_p' t^{1/2}$ represents the oxygen pickup in forming adherent oxide according to a

parabolic rate law, and the term $K_v t$ represents metal evaporation either as metal or oxide according to a linear law. These two models are characterized by its simplicity and physical significance. Many studies extracted the rate constants from these two linear kinetic models. They will also be used in this study for the purpose of comparison.

B. Modified Tedmon's Non-linear Model

Tedmon's model given in Table 4 gives the relationship between the reaction time t and the instantaneous scale thickness X and both K_d and K_s are parameters in terms of the scale thickness. The model equation is essentially based on the assumption of continuous and uniform scale thickness. However, these assumptions are rarely encountered in practice (35), especially for the assumption of uniform scale thickness for alloys forming Cr_2O_3 layer. In addition, the instantaneous scale thickness in Tedmon's model (Table 4) is not readily available from the experimental work to calculate the unknown parameters in that model equation. Therefore, an attempt to modify Tedmon's model by replacing the instantaneous scale thickness with the directly measurable sample weight gain per unit area was made in this investigation. This procedure gives the global parabolic rate constant and the volatilization rate in terms of the weight gain per unit area, which is the sum due to the oxygen

pickup reaction and the volatilization effect. The overall model equation is given by

$$t = \frac{K_p''}{K_v^2} \left\{ -\frac{K_v}{K_p''} W - \ln \left(1 - \frac{K_v}{K_p''} W \right) \right\} \quad (9)$$

where K_p'' = one half of the global parabolic rate constant K_p
($\text{gm}^2/\text{cm}^4\text{-sec}$)

K_v = volatilization rate constant ($\text{gm}/\text{cm}^2\text{-sec}$)

W = weight gain per unit area (gm/cm^2)

t = time (sec)

The calculation of K_p'' and K_v in the above non-linear equation was made by using the experimental results so that the optimal value of both parameters can be simultaneously solved with the modified Gauss-Newton iteration method (8). The following equations are used in order to calculate the increment of K_p'' and K_v during the iteration step.

$$\frac{\partial t}{\partial K_p''} = -\frac{1}{K_v^2} \ln \left(1 - \frac{K_v}{K_p''} W \right) - \frac{W}{K_v (K_p'' - K_v W)} \quad (10)$$

$$\frac{\partial t}{\partial K_v} = \frac{W}{K_v^2} + \frac{2K_p''}{K_v^3} \ln \left(1 - \frac{K_v}{K_p''} W \right) + \frac{K_p'' W}{K_v^2 (K_p'' - K_v W)} \quad (11)$$

The calculation was performed by using a SAS (Statistical Analysis System) program given in Appendix A. Since the SAS program can only print the floating point results as small as 10^{-8} , which is obviously too large as

compared with the typical K_p'' values (app. 10^{-13} gm²/cm⁴-sec), the dimension of K_p'' and K_v has been changed to $K_p'' [=]$ gm²/m⁴-hr and $K_v [=]$ gm/m²-hr during the calculation. Accordingly, a division factor of 3.6×10^{11} is needed in order to change the printout value of K_p'' to the CGS system; a division factor of 3.6×10^7 is needed in order to change the printout value of K_v to the CGS system. The initial value of K_p'' and K_v for this iterative phase were estimated from experience. The optimal value of K_p'' and K_v are obtained when the residual sum of square calculated from the current parameter values differ from the last one by less than 10^{-8} . The 95% confidence intervals of the estimated parameters were obtained from the SAS program. The Marquardt method also has been used to check the results of several calculations. Good agreements were found from them, although the Marquardt method usually takes more iteration steps. The main feature of this procedure is that it enables the K_p and K_v to be simultaneously and directly calculated from the experimental data, instead of calculating K_p from Hagel's K_v correlation as in the study of Giggins and Pettit (52) where the uncertainty of K_v influences the accuracy of the K_p estimation.

The experimental data for analysis were taken from the recorder chart paper for every 0.5 hour in the first five hours and 2.5 to 5 hours for the subsequent times. All of

the experimental data at 900°C or above were analyzed using the modified Tedmon's model equation (9) and models no. 4 and 5 in Table 4. This was done since the Cr_2O_3 volatilization effect is significant above this temperature although no net weight losses were observed (30,52,97). At temperatures below 900°C, or when the reaction time is short, satisfactory results are obtained using the parabolic rate law. The K_p and K_v calculated from the modified Tedmon's model using the above mentioned numerical method is believed to be accurate since no linearization treatment has been done on the model equation. The rate data obtained from this procedure will be further discussed and compared with other studies in the following sections.

V. RESULTS AND DISCUSSION

A. Sulfidation-Oxidation of Iron-Based Superalloys and Pure Chromium

1. Sulfidation-oxidation of Armco 18SR alloys

Sulfidation-oxidation of 3 different heat treated Armco 18SR alloys has been conducted at atmospheric pressure between 750-1100°C. The effect of the flow rate and SO_2/O_2 ratio on the reaction rate will be discussed in section (V-A-4). The reaction rate in a slowly flowing (60 ml/min at 25°C) and equimolar SO_2/O_2 environment will be presented and discussed in this section.

For Armco 18SR alloy, the corrosion rate at 750°C is too small to be accurately detected and will not be included in the data analysis. At higher temperatures, the reaction followed parabolic kinetics and the volatilization of Cr_2O_3 scale by the formation of CrO_3 must be taken into account. Formation of Cr_2O_3 scale was substantiated by X-ray diffraction analysis discussed in section (V-A-5). More discussions about the volatilization of Cr_2O_3 on different heat treated Armco 18SR alloys and other similar studies will be made in section (V-B-2). The weight gain curves of this study are shown in Figure 6 and Figure 7. Table 5 gives the parabolic rate constant and volatilization constant calculated from the non-linear modified Tedmon's kinetic

Figure 6. Sample weight gain curve for Armco 18SR-A as a function of time and temperature.

Figure 7. Sample weight gain curve for Armco 18SR-B and Armco 18SR-C as a function of time and temperature.

model (I) and from two other linear kinetic models (II and III). The R^2 statistic for linear models also has been included. Figure 8 shows the parabolic rate constant at different reaction temperatures with a 95% confidence interval for each experimental point. The results show that Armco 18SR-A alloy always shows a higher reaction rate than 18SR-B and 18SR-C. The difference is more obvious at the low temperature region. The scales formed on 18SR-B and 18SR-C are adherent and compact whereas flaked scale has been observed on 18SR-A during cooling to room temperature. This indicates that the effect of heat treatment on the alloys with the same chemical composition is an important factor for corrosion resistance purpose.

The experimental parabolic rate constants have been fitted using the Arrhenius equation. For Armco 18SR-A it gives

$$K_p = 3.70 \times 10^{-7} \text{ Exp}(-28727 \pm 2030/RT) \quad (\text{gm}^2/\text{cm}^4\text{-sec}) \quad (12)$$

with R^2 statistic equal to 0.9901. The corresponding experimental data for Armco 18SR-B and C give

$$K_p = 10.77 \text{ Exp}(-78412 \pm 6108/RT) \quad (\text{gm}^2/\text{cm}^4\text{-sec}) \quad (13)$$

with R^2 statistic equal to 0.9763. The K_p values of 18SR-B and 18SR-C are fitted together due to the similar heat treatment for both alloys (section III-A).

Table 5. The parabolic rate constant (K_p) and the volatilization rate constant (K_v) calculated from different kinetic models.*

Sample	T (C)	K_p (gm ² /cm ⁴ -sec) **			
		I	II	III	IV
18SR-A	750	-	-	-	2.64E-13
	900	1.52E-12	1.84E-12	1.51E-12	-
	1000	5.36E-12	4.88E-12	1.61E-12	-
	1100	8.60E-12	1.25E-11	7.98E-12	-
18SR-B	900	3.78E-14	5.60E-14	2.87E-14	-
	1000	3.02E-13	5.41E-13	2.85E-13	-
	1100	5.89E-12	6.93E-12	5.89E-12	-
18SR-C	900	2.28E-14	4.22E-14	7.11E-15	-
	1000	2.86E-13	5.25E-13	2.41E-13	-
	1100	2.74E-12	1.52E-12	3.04E-12	-
T310	750	-	-	-	1.09E-13
	900	2.04E-12	1.08E-12	1.89E-12	2.09E-12
	1000	7.65E-12	8.88E-12	6.48E-12	-
	1100	2.38E-11	7.89E-12	7.86E-12	-
Cr	750	-	-	-	7.87E-14
	820	-	-	-	4.03E-13
	900	-	-	-	5.82E-12
	1000	-	-	-	1.95E-11

* Under the condition of $SO_2/O_2 = 1$ and flow rate = 60 ml/min (25°C).

** I : Modified Tedmon's model equation (9) in the text.

II : $W = K_p t^{1/2} - K_v t$ where $K_p = (K_p')^2$

III: $W = K_p t^{1/2} - K_v t + C$ where $K_p = (K_p')^2$

IV : $W^2 = K_p t$

K_y (gm/cm ² -sec) **			R^2		
I	II	III	II	III	IV
-	-	-	-	-	.9569
5.55E-10	7.00E-10	4.45E-10	.9985	.9988	-
2.27E-09	4.30E-09	2.43E-09	.9591	.9803	-
4.78E-09	4.49E-09	3.07E-09	.9920	.9943	-
4.83E-10	3.79E-10	2.78E-10	.9740	.9905	-
8.61E-10	1.05E-09	4.39E-10	.9757	.9868	-
1.43E-09	1.52E-09	1.09E-09	.9991	.9993	-
3.57E-10	3.51E-10	1.08E-10	.9451	.9804	-
1.14E-09	1.18E-09	4.87E-10	.9654	.9841	-
2.01E-09	6.79E-10	1.74E-09	.9894	.9945	-
-	-	-	-	-	.9651
2.22E-10	-	-	.9972	.9984	.9963
5.18E-10	1.06E-09	4.56E-10	.9987	.9993	-
3.40E-09	-	-	-	-	-
-	-	-	-	-	.9946
-	-	-	-	-	.9943
-	-	-	-	-	.9908
-	-	-	-	-	.9999

Figure 8. Temperature dependence of the parabolic rate constant for Armco 18SR alloys. The 95% confidence interval of each experimental point is given by the error bars.

Comparison of the present work with previous studies is difficult due to limited available corrosion information on this alloy. Perkins and Bhat (128) investigated the corrosion behavior of many sulfidation-resistant alloys for coal gasification service using high sulfur potential gas mixtures. Their test results on Armco 18SR alloy have no information on its parabolic rate constant and activation energy. However, the results (128) of formation of adherent oxide are consistent with the present study. Perkins and Bhat (128) also reported 3.2×10^{-4} gm/cm² to 4.5×10^{-4} gm/cm² of weight change after a 24-hour reaction at 1800°F. This result is comparable with the present study of Armco 18SR-A at 1000°C which gives about 4×10^{-4} gm/cm² from interpolation in Figure 6. Although no heat treatment history was reported by Perkins and Bhat (128) for Armco 18SR alloys, it is believed that 18SR-A was what they used for their corrosion test. The activation energies of the present investigation cannot be compared with the other studies because no such data on the same alloy has been reported. However, wide differences of the activation energy for the similar Fe-Cr alloy at different temperature ranges have been reported (95,113).

The parabolic rate constant for the Armco 18SR can be compared with the result on Fe-18Cr alloy by Kuse et al. (95). From Table 2 (section III-A), it is found that the

major difference in chemical composition between Armco 18SR and the Fe-18Cr alloy is the 2% of Al in the Armco 18SR alloy. The addition of Al in this type alloy has been proven to be beneficial in improving corrosion resistance, especially in a sulfidizing environment (128). In this investigation, the parabolic rate constant of 18SR-A at 1000°C is $5.36 \times 10^{-12} \text{ gm}^2/\text{cm}^2\text{-sec}$ which is slightly smaller than $7 \times 10^{-12} \text{ gm}^2/\text{cm}^2\text{-sec}$ obtained by Kuse et al. (95) in air. The beneficial effect of Al was obvious when compared with Armco 18SR-B and C since an order of magnitude decrease of the parabolic rate constant was obtained from this investigation at 1000°C.

2. Sulfidation-oxidation of Armco T310 alloy

The Armco T310 alloy has been studied in slowly flowing (60 ml/min at 25°C) and equimolar SO_2/O_2 gas mixtures. The weight gain curve of the experimental work is shown in Figure 9. Table 5 (section V-A-1) gives the parabolic rate constant and several volatilization rates calculated from different kinetic models. It was found that the corrosion rate of T310 is greater than that of 18SR alloys under the same experimental conditions. The scale formed on T310 is not so adherent as in 18SR-B or 18SR-C since it flakes off on cooling from the reaction temperature at 900, 1000 and 1100°C. At 1100°C the scale flaked like fine powder whereas

Figure 9. Sample weight gain curve for Armco T310 as a function of time and temperature.

at 900 and 1000°C the scale flaked in strip form.

Metallographic investigation of the flaked scale will be presented in section (V-A-5). The parabolic rate constant calculated from the weight gain curve is given in Figure 10. The parabolic reaction rates are fitted to the Arrhenius equation as

$$K_p = 1.835 \times 10^{-4} \text{ Exp}(-43028 \pm 1415/RT) \text{ (gm}^2\text{/cm}^4\text{-sec)} \quad (14)$$

with the R^2 statistic equal to 0.9978. In general this alloy is not so effective as the Armco 18SR alloys, especially 18SR-C, in SO_2/O_2 corrosive environments. The presence of Ni in the alloy will increase the strength in the austenitic Fe-Cr-Ni alloy. Nickel is also an important element for the control of strength and ductility of the alloy. However, the presence of Ni will increase the chance of forming liquid sulfide slags, especially for the high sulfur potential coal gasification environment where a heavily sulfidized and carburized product can be found beneath the oxide layer (128). In this investigation, the equilibrium sulfur potential calculated from Appendix B ranged from 10^{-29} to 10^{-20} atmosphere for temperatures between 750 and 1100°C. These values are too small for the formation of either NiS or Ni_3S_2 as indicated by the available equilibrium diagram (182). The equilibrium diagram of Natesan and Chopra (118) also indicates the impossibility of formation of the sulfide

Figure 10. Temperature dependence of the parabolic rate constant for Armco T310. The 95% confidence interval of each experimental point is given by the error bars.

phase when the sulfur activity is less than 10^{-11} atm at 875°C. However, the sulfide phase was observed at temperatures above 1000°C from the metallographic examination. This could be due to the kinetic reason in which the sulfur-bearing compound migrates to the low oxygen activity place beneath the outer oxide layer either by dissolution mechanism or by diffusional transport through the pores or cracks in the scale. The equilibrium oxygen potential in this investigation (0.43-0.49 atm between 750-1100°C) is high enough for NiO to be initially formed during the reaction. The formation of the small amount of NiO and gamma-Fe₂O₃ in addition to the main Cr₂O₃ phase was substantiated by X-ray diffraction analyses and metallographic examinations. This was believed to partly contribute to the higher corrosion rate than the Armco 18SR alloys. Danielewski and Natesan (31) studied the oxidation-sulfidation behavior of Fe-Cr-8Ni alloys in multicomponent gas mixtures that contained CO, CO₂, CH₄, H₂ and H₂S. They found that for a given sulfur activity, the oxygen activity required for the formation of a continuous oxide layer in an Fe-22Cr-8Ni alloy was approximately 10^2 and 10^3 times that calculated for Cr-Cr₂O₃ equilibrium at temperatures of 875 and 750°C, respectively. This phenomena was not observed in the present study. This is probably due to the higher Ni content in the alloy of the present study as

compared with the alloy used by Danielewski and Natesan (31) that results in a higher chance of liquid slagging during the reaction.

3. Sulfidation-oxidation of Cr metal

Sulfidation-oxidation of chromium at the same experimental conditions as in the above sections has been carried out from 750 to 1000°C. The reaction times are usually shorter than in the alloy system but are comparable or longer than the previous investigations for the oxidation of chromium (56,59). The weight gain curves shown in Figure 11 were analyzed using the parabolic rate law. The rate constant has been given in Table 5 (section V-A-1). The parabolic plot of the experimental data and the corresponding R^2 statistic are shown in Figure 12. Good correlation with parabolic rate law is indicated.

Although many investigators studied the sulfidizing-oxidizing behavior of Ni, Co, Fe and Cu by thermogravimetric method, little is known about the corrosion behavior of chromium in sulfidizing-oxidizing gas environment. Romeo and his coworkers (149,150) studied the effect of pre-existing oxide on the high temperature sulfidation of chromium. They reported several orders of magnitude increase in the diffusivity of Cr in Cr_2O_3 when exposing the initially present oxide to sulfur-bearing atmospheres at very low

Figure 11. Sample weight gain curve for Cr as a function of time and temperature.

Figure 12. Parabolic plot of the pure Cr, Arco 18SR-A and Arco T310 at a gas composition of $\text{SO}_2:\text{O}_2$ equal to 1.

oxygen partial pressures (150). Since their experimental procedure is different from the present study, the results are very hard to compare. The experimental parabolic rate constants of the present investigation are compared with Gulbransen and Andrew (56) and Hagel (59) as shown in Figure 13. Both of these studies (56,59) are under pure oxidative environments with oxygen pressure equal to 0.1 atmosphere. The parabolic rate constants in the present investigation were correlated with the Arrhenius equation as

$$K_p = 0.45 \text{ Exp}(-59671 \pm 6424/RT) \quad (\text{gm}^2/\text{cm}^4\text{-sec}) \quad (15)$$

with the R^2 statistic equal to 0.9773. The activation energy in this study, 59671 cal/mole, is very close to that reported by Hagel (59) which is 59000 ± 1800 cal/mole. The uncertainty limit of the above equation will overlap with the confidence intervals reported by Hagel (59). Figure 13 indicates that the parabolic rate constants of this investigation are greater than the results of Hagel (59) and Gulbransen and Andrew (56). Since the flaked solid product formed in all cases are Cr_2O_3 which is a P - type semiconductor (94), the higher oxygen partial pressure of this study (327-370 mm Hg, depending on the reaction temperature) was considered to contribute to the higher corrosion rate than the lower oxygen pressure (76 mm Hg) of the studies by Hagel (59) and Gulbransen and Andrew (56).

Figure 13. A comparison of the experimental results on the sulfidation-oxidation of pure Cr with reported oxidation results from the literature.

Similar phenomena have been indicated by Kofstad and Hed (86) who found that the oxidation of Co-25Cr from 900 to 1300°C gave the parabolic rate constant as $1/4$ to $1/3$ power of the oxygen pressure when the oxygen pressure was greater than 100 torr. Other evidence comes from the study of Kuse et al. (95) on the high temperature oxidation of Fe-18Cr sealing alloy. They (95) found the oxidation rate constant changes in proportion to the exponent of $1/5$ of the partial pressure of oxygen. Kuse et al. (95) identified the oxide films as virtually consisting of Cr_2O_3 . Caplan et al. (28) studied the oxidation of chromium at 890-1200°C. They found that surface preparation has a large effect on scaling.

The use of chromium as an alloying element has been known to be beneficial to corrosion resistance for many years. However, the failure of pure chromium in oxidation has been characterized by Gulbransen and Andrew (56) as the 'breakdown' phenomena during the reaction. This phenomenon is attributed to the development of the rapid reaction in which ionic diffusion processes within the scale are no longer rate controlling. No rate controlling step was identified during the breakdown phenomena. However, poor adhesion of the oxide scale to the metal is observed for these conditions. The failure of Cr in oxidation was explained to be related to the high vapor pressure of Cr at temperatures above 900°C (56). Similar phenomena have been

obtained in this study but not as clearly defined as the results obtained by Gulbransen and Andrew (56). The scale was found to flake off on cooling around 1000°C which is similar to the result of Gulbransen and Andrew (56) above 1025°C. The flaked scales at 1000°C were analyzed using the X-ray diffraction method. Only Cr_2O_3 solid products were identified. The Cr_2O_3 condensed phase was obtained since the oxygen potential of this experiment ranged from 0.43 to 0.49 atmosphere which is much higher than the equilibrium oxygen pressure (10^{-24} atm at 1200°K) between Cr and Cr_2C_3 .

4. Effect of flow rate and sulfur activity

The effect of flow rate on the corrosion rate of Armco 18SR-C at 1100°C was carried out. Armco 18SR-C has the best corrosion resistance of the Armco 18SR alloys. The higher the reaction temperature the better the chance to maintain the gaseous film transport controlled condition which in turn influences the volatilization rate. The effects of flow rate on the experimental parabolic rate constant and the volatilization rate constant are shown in Figure 14. It was found that increasing the total flow rate four times showed no significant increase in the volatilization rate. The flow condition in the reaction column remained in the natural convection condition despite an increase in the flow rate. The large diameter of the reactor column makes it difficult

Figure 14. Effect of flow rate on the parabolic rate constant and the volatilization rate constant of Armco 18SR-C. The 95% confidence interval of each experimental point is given by the error bars.

to attain the forced convection conditions without supplying a large amount of reacting gases which introduces more electronic noise on the recorder. Compared with the other experimental conditions, the linear velocity under the maximum flow rate of the present investigation is 0.135 cm/sec which is quite small as compared with the forced convection condition of Davis et al. (32) where 12 cm/sec of linear velocity was reported by using a small diameter tube.

The effect of sulfur activity on Armco 18SR-C alloy has been done at 1100°C by varying the SO_2/O_2 ratio from 1, 4, 8 to 12. The SO_2/Ar mixture and pure sulfur dioxide were also used. The sulfur activity was increased from 9×10^{-21} atm to 2×10^{-18} atm as $\text{SO}_2:\text{O}_2$ increased from 1 to 12. Figure 15 shows the effect of SO_2/O_2 ratio on the experimental parabolic rate constant and the volatilization rate constant. The unvarying trend of both rate constants proves the very good corrosion resistance of Armco 18SR-C alloy under the present experimental range. The constant trend of the parabolic rate constant is also consistent with the earlier results (120,178) which indicated that the rate of attack of the steel was largely independent of the gas composition when using SO_2 and O_2 gas mixtures.

The attack on pure chromium under simultaneous sulfidizing and oxidizing atmospheres has been scarcely investigated although the corrosion kinetics under each

Figure 15. Effect of SO_2/O_2 ratio on the parabolic rate constant and the volatilization rate constant of Armco 18SR-C. The 95% confidence interval of each experimental point is given by the error bars.

condition has been extensively studied. The effect of sulfur activity on pure chromium was carried out at 900°C by the same procedure as on Armco 18SR-C. The reaction temperature was limited to 900°C due to the occurrence of a 'breakdown' phenomena around 1000°C as reported by Gulbransen and Andrew (56). In addition, 900°C is close to the operating temperature of gas turbine where chromium is one of the important alloying elements. The equilibrium sulfur partial pressures of the present study are in the range of 1.5×10^{-25} atm to 2.5×10^{-23} atm when $\text{SO}_2:\text{O}_2$ is increased from 1:1 to 8:1 at 900°C. Figure 16 shows the weight gain curve for the 50 hour run. The reaction curves indicate that the rate law can change more than once during the reaction. Since most of the earlier studies limited the experimental data to very short time periods, no comparison with previous studies can be made. Hagel's (59) pure oxidation rate curve under 0.1 atm of oxygen pressure is shown in Figure 16 for comparison of data from the short term experiments. It can be shown that the short time (<5 hr) weight gain curve of Figure 16 indicates that the increasing sulfur activity will increase the initial rate. However, this proportionality does not hold for the longer experimental times. This behavior indicates that the SO_2/O_2 ratio is not a controlling factor on the rate during the latter stage of the reaction. A possible explanation is that the metal-scale separation

Figure 16. Sample weight gain curve for Cr as a function of time and SO_2/O_2 ratio.

during the reaction renews the reaction surface and, therefore, starts the new parabolic rate law. The addition of 0.9 wt.% of yttrium in the chromium sample has been reported to improve the oxide adherence when Y_2O_3 and $YCrO_3$ are formed at high temperatures but does not influence chromium oxide growth (59).

5. Metallographic investigation

The characterization of the corrosion products in the present investigation was performed using X-ray diffraction method and optical microscopy. The Armco 18SR-B and 18SR-C alloys formed an adherent scale at all temperatures under the SO_2/O_2 atmosphere. The scale formed on Armco 18SR-A was found to flake off on cooling from 1000°C. The same phenomenon was observed for pure chromium where the scale was found to flake off on cooling from 900°C. The X-ray diffraction patterns of these flaked samples are the same. Table 6 gives the comparison between the calculated d-spacing between the different crystal planes and their intensity with the corresponding standards from the American Society for Testing and Materials (5). Rhombohedral Cr_2O_3 was found to be the only compound in the flaked scale. The scale formed on Armco T310 is also not very adherent on cooling from 900, 1000 and 1100°C. At 1100°C, the flaked scale was found to give a complex X-ray diffraction pattern. A mixture of Cr_2O_3 ,

Table 6. Comparison between the X-ray diffraction pattern of the present work with the ASTM standard (5).

(I). Sources: Flaked scale from 18SR-A and Cr at 1000°C.

	d(A)	3.670	2.675	2.495	2.188	1.833	1.684	1.433
This work								
	I/I ₀	M	S	S	W	W	S	W
	d(A)	3.633	2.666	2.480	2.176	1.816	1.672	1.431
Cr ₂ O ₃ standard								
	I/I ₀	75	100	95	40	40	90	40

Table 6. (continued)

(II). Source: Flaked scale from T310 at 1100°C.

This work	d(A)	4.85	3.62	2.98	2.66	2.54	2.48	2.17	2.11
	I/I ₀	W	S	S	S	S	S	M	M
Mixture of Cr ₂ O ₃ , γ-Fe ₂ O ₃ and NiO ²	d(A)						2.41 ²		2.09 ²
		4.84 ¹	3.63	2.95 ¹	2.67	2.52 ¹	2.48	2.18	2.09 ¹
	I/I ₀						91 ²		100 ²
		40	75	>100	100	>100	95	40	>100 ¹

d(A)	1.81	1.72	1.67	1.62	1.49	1.46	1.43	1.30
I/I ₀	S	M	S	M	S	M	M	W
d(A)	1.82	1.70 ¹	1.67	1.61 ¹	1.48 ²	1.47	1.43	1.30
I/I ₀	40	>100	90	>100	57	25	40	20

gamma-Fe₂O₃ and NiO was identified from the pattern. The comparison between the d-spacing and the intensity of this work with the standards (5) is given in Table 6. The 6 strongest intensity lines of gamma-Fe₂O₃ and the 3 strongest intensity lines of NiO are employed for this comparison.

Optical microscopic investigation of the scale has been done on each sample after experiments. A picture of 1000 magnification for each sample was obtained from this procedure. The typical temperature dependencies of the morphology of Armco 18SR alloys are given from Figures 17 to 19. The upper black region represents the mounting material. The lower blank area represents the unaffected alloy. The scale products are located near the center of each picture. For Armco 18SR-A, uneven scale thickness was found at all temperatures in the present investigation. Small amounts of localized oxide inclusions (white matrix in the base alloy) are found for 18SR-A and 18SR-B at 1000-1100°C (Figures 17, 18). In addition, Armco 18SR-A showed localized deep penetrations of oxides at random locations on the alloy surface. Similar results have been found by Perkins and Bhat (128). This was attributed to the high local titanium concentration in the alloy which causes the titanium nitrides, carbides etc. to be oxidized selectively just below the surface and pools of internal oxidation products are formed (128). In comparison with the other samples, Armco

Figure 17. 1000X. Sulfidation-oxidation($\text{SO}_2/\text{O}_2=1$) of Armco 18SE-A at 750°C(left) and 1100°C(right).

Figure 18. 1000X. Sulfidation-oxidation($\text{SO}_2/\text{O}_2=1$) of Armco 18SR-B at 750°C(left) and 1100°C(right).

Figure 19. 1000X. Sulfidation-oxidation($\text{SO}_2/\text{O}_2=1$) of Armco 18SR-C at 750°C(left) and 1100°C(right).

18SR-C is the best among the 18SR alloys since a very adherent, even and compact scale was developed during the reaction. Figure 20 shows that no oxide or sulfide penetration was formed in the 18SR-C when the $\text{SO}_2:\text{O}_2$ ratio was increased from 1:1 to infinity (pure SO_2). However, few localized oxide penetrations on the alloy surface were found in Armco 18SR-B, especially at temperatures above 1000°C .

The morphologies of the Armco T310 alloy at different temperatures are typified by Figure 21. Although a very small amount of internal oxidation was found along the grain boundaries at 750°C , the corrosion resistance at 750°C is very good since an even scale of Cr_2O_3 was developed during the reaction. At 1100°C , however, the reaction rate increased significantly (Figure 9). The flaked scale at 1100°C has been identified by X-ray diffraction as a mixture of Cr_2O_3 , gamma- Fe_2O_3 and NiO . The increased corrosion rate at 1100°C is due to the formation of the liquid sulfide slag during the reaction. Figure 21 indicates the sulfide phase in the center of the picture. The oxide phase (black matrix) was surrounded by the sulfide phase. Compared with the morphology at 750°C , large pools of internal oxidation and sulfidation are found either beneath the scale or penetrating to a significant depth. Perkins and Bhat (128) studied the corrosion of 310 SS in $\text{H}_2\text{S}-\text{H}_2\text{O}$ atmospheres at 1800°F and found at some critical $\text{H}_2\text{O}:\text{H}_2\text{S}$ ratio a liquid sulfide slag.

Figure 20. 1000X. Sulfidation-oxidation of Armco 18SR-C at 1100°C under $\text{SO}_2/\text{O}_2=1$ (left) and pure SO_2 (right).

Figure 21. 1000X. Sulfidation-oxidation($\text{SO}_2/\text{O}_2=1$) of Armco T310 at 750°C(left) and 1100°C(right).

Samples were attacked severely in less than 24 hours. A similar structure as shown in Figure 21 was obtained by Perkins and Bhat (128). Their results on the formation of spalled oxides are also consistent with the present investigation using SO_2/O_2 as the corrosion gases. The scale thickness developed on the alloys during the reaction is summarized in Table 7.

The morphology of chromium under SO_2/O_2 atmospheres is shown in Figure 22 for different temperatures and Figure 23 for different sulfur activity. At 750°C , an even scale of chromium oxide was developed with a very small amount of sulfide beneath the outer oxide layer. Internal oxidation was found by penetrating the alloy up to a depth of at least 45 microns. The Cr_2O_3 scale was found to flake off on cooling from 900 and 1000°C . The flaked scale at 1000°C , retained in the picture by special treatment, is indicated by the upper dark gray area surrounded by the black voids (Figure 22). The high porosity of the product scale is evident. The center light gray area indicates the sulfide phase with some oxide islands near the outer edge of the sulfide layer. Deep penetration of sulfide and oxide inclusions along the grain boundaries also can be observed. The enhanced corrosion was due to the penetration of the sulfur species through the outer porous oxide layer to a place where the oxygen activity is very low so that the

Table 7. Average scale thickness on sulfidation-oxidation of Armco alloys.

Alloy	Temp (C)	Thickness (micron)	Remarks on scale ¹
18SR-A	750	1-2	UEV, LP, AO
	900	1-3	UEV, LP, AO
	1000	2-9	UEV, LP, IO, SO
	1100	2-9	UEV, LP, IO, SO
18SR-B	750	1	EV, AO
	900	2.5	EV, AO
	1000	3	FLP, AO
	1100	5	FLP, AO
18SR-C	750	4.5	EV, CP, AO
	900	5	EV, CP, AO
	1000	5	EV, CP, AC
	1100	8	EV, CP, AO
T310	750	1	EV, AO
	900	1-2	UEV, IC, SO
	1000	2-5	UEV, LP, IO, SO
	1100	5-10	UEV, LP, EIO, SO

¹AC : Adherent oxide.
 CP : Compact scale.
 EIO: Enhanced internal oxidation.
 EV : Even scale.
 FLP: Few localized penetration.
 IO : Internal oxidation.
 LP : Localized penetration.
 SO : Spalled oxide.
 UEV: Uneven scale.

Figure 22. 1000X. Sulfidation-oxidation($\text{SO}_2/\text{O}_2=1$) of pure Cr at 750°C (left) and 1000°C (right).

Figure 23. 1000X. Sulfidation-oxidation of Cr at 900°C under $\text{SO}_2/\text{O}_2=1$ (left) and pure SO_2 (right).

formation of sulfide phase is feasible. Once the sulfide layer is formed, the transport of chromium cations through the liquid sulfide slag was accelerated and hence the increased corrosion rate. In the study by Romeo et al. (149,150) where an $\text{H}_2\text{S}-\text{H}_2$ gas mixture was reacting with preoxidized chromium, a much thicker layer of sulfide was formed in comparison with the present study. They also reported that chromium sulfide can be found on both sides of the oxide layer initially present, with the outer portion of the sulfide scale much thicker than the inner portion (150). The high sulfur activity of 1.5×10^{-5} atm (149) using 10% $\text{H}_2\text{S}-\text{H}_2$ gas mixtures in their study is probably the reason for the thicker sulfide layer as compared with the present investigation using an SO_2/O_2 mixture where only 10^{-22} atm of sulfur activity prevailed. The sulfur activity dependence of chromium in SO_2/O_2 atmospheres is characterized by Figure 23. It is evident from Figure 23 that more sulfide inclusions connected by thin stringers were found in pure SO_2 atmosphere than in SO_2/O_2 atmosphere.

B. High Temperature Gas-Solid Reactions with Formation of Volatile Species

High temperature reactions between a gas and solid to form a volatile product have very important practical applications in the design of materials for fossil, solar,

and nuclear power reactors and aircraft engines. The formation of volatile species also plays an important role in the refinement and production of certain metals as well as in the kinetics of some high temperature corrosion systems. Generally the kinetics of this kind of reaction is different from the ordinary gas-metal corrosion reactions in which the ionic diffusional transport through the solid product layer controls the overall rate. Since the reaction products are volatile, the reaction rate is primarily governed by the process at the gas-solid interface or within the boundary layer. Recent studies on different reaction/volatilization systems have been reported by Zaplatynsky (206), Gulbransen and Andrew (57), Kohl et al. (87) and Fryburg et al. (49). Although the importance of the formation of volatile species in many of these high temperature studies is recognized, the kinetics of this kind of reaction has only been investigated to a limited extent. This is probably due to the experimental difficulties as discussed by Gulbransen and Andrew (57).

The investigation of gas-solid reaction with formation of volatile species using convective diffusional theory and surface reaction rate was first developed in 1967 by Bartlett (11), who tried to correct the commonly accepted misconception that gaseous diffusion is kinetically important only when the surface reaction rate is very fast. As a

result, many previous investigators had ignored the diffusional effect of the volatile species in studying the reaction mechanism. Bartlett (11) presented a kinetic treatment of the platinum oxidation reaction by considering simultaneously the convective diffusion rate of the product gas PtO_2 through the gaseous boundary layer and the surface chemical reaction rate. By equating these two rate expressions at steady state condition and applying the Hertz-Langmuir equation, derived from the kinetic theory of gases, for the backward rate constant, the following model equation was obtained:

$$\text{Rate} = \frac{(M_0/\rho) (2\pi MRT)^{-0.5} K P_{O_2}}{1 + (2\pi MRT)^{-0.5} P_t/k_m} \quad (16)$$

where M_0/ρ = factor to convert molar oxidation rate to a surface recession rate obtainable from experiment.

M = molecular weight of volatile specie PtO .

K = equilibrium constant of Pt oxidation reaction.

P = total pressure.

k_m = mass transfer coefficient.

The basic assumptions of the model equation are that the vapor pressure of the volatile species beyond the boundary layer is negligible and the condensation coefficient of the

volatile species on the solid surface is equal to one. The general model can be simplified to the two limiting cases (11):

(1) When $1 \ll (2\pi MRT)^{-0.5} P_t / k_m$, equation (16) reduces to

$$\text{Rate} = (M_0/\rho) K k_m P_{O_2} / P_t \quad (17)$$

for PtO_2 transport controlled at high total pressures.

(2) When $1 \gg (2\pi MRT)^{-0.5} P_t / k_m$, equation (16) reduces to

$$\text{Rate} = (M_0/\rho) (2\pi MRT)^{-0.5} K P_{O_2} \quad (18)$$

for surface reaction controlled at very low total pressures.

Bartlett compared this model with Fryburg's natural convection experimental data (48,50) on the oxidation of platinum. Good results over a large pressure range were observed. The significance of the model is that it allows the theoretical rate to be calculated independently of the experimental rate if the reaction equilibrium constant and the mass transfer coefficient are available. The mass transfer coefficient can be calculated from the Nusselt number by using accepted dimensionless fluid correlation if the gas transport properties can be reasonably estimated. After Bartlett's investigation, several studies were made to apply this model to other reaction systems. These include the oxidation of platinum in forced convection conditions

(122) and the oxidation of iridium in both natural convection and forced convection systems (197,198). One important result of the former study (197) was to demonstrate that the model is valid for any system for which the mass transfer coefficient can be calculated, regardless of whether or not heat transfer is involved.

In addition to these cases, it was found that several other gas-solid reactions with simultaneous formation of volatile species can be reinterpreted with Bartlett's model (section 1). These include some earlier studies that reported the experimental results but gave no explanation of the reaction mechanism, and several recent studies that reported the experimental results and the reaction mechanism but gave no predictive rate model for the particular reaction system. The experimental results of volatilization of several superalloys from the first part of this investigation are also presented (section 2). The experimental results are compared with the prediction from the mass transfer calculation using the Chapman-Enskog equation and the empirical combining rules for calculating the high temperature gaseous diffusion coefficient. The empirical combining rules allow the force constants for a pair of different species to be derived from the individual ones (15). The results of the first two sections are further assessed with the high temperature gaseous diffusion theory

(section 3) as a basis for comparison.

1. Reevaluation of previously reported experimental data

a. Oxidation of chromium oxide Pure chromium and its alloys of Fe, Co and Ni always form the Cr_2O_3 solid products at high temperatures. The formation of a continuous Cr_2O_3 protective layer in the alloy is attributed to the selective oxidation of chromium at high temperatures. The present practice is to maintain a chromium content of at least 18%. When the oxidation period is long, deviation from parabolic rate law to linear rate law occurs. This is generally attributed to the volatilization of reaction product by the following reaction (27,53,59,104,170,179):

Although many investigators believe that the above reaction takes place whenever Cr_2O_3 is formed on the outer layer of the metal and the reaction rate is independent of the scale thickness at any time during the reaction, few people before Graham and Davis (53) had ever systematically studied the mechanism of this reaction. Graham and Davis (53) studied the oxidation/vaporization kinetics of Cr_2O_3 at 1200°C and oxygen pressure between 10^{-4} and 1 atmosphere. The flow rate and total pressure dependency of the reaction rate showed that the mass transfer of CrO_3 through a laminar boundary layer controls the reaction rate. Based on the film

theory, their model equation predicted that the rate is $3/4$ power of the oxygen partial pressure, first power of the diffusion coefficient and inversely proportional to the boundary layer thickness. Their work in checking the order dependence of the rate equation gave satisfactory results. Two points, however, need further discussion.

(1) The only numerical quantitative comparison between their model prediction and the experimental data was through the boundary layer thickness calculation using the following dimensionless equation for mass transfer on a flat plate:

$$\frac{h_M L}{D_{12}} = \frac{k_M L}{D_{12}} \frac{RT}{P_t} = 0.664 Sc^{1/3} Re^{1/2} \quad (20)$$

The not so small difference between the calculated value and the experimental data as indicated in their paper (53) is probably due to the inaccuracy of equation (20) and, in a more significant way, due to the inappropriate prediction of the diffusion coefficient D_{12} in equation (20).

If the Lennard-Jones parameter of $\sigma = 4.5 \text{ \AA}$ and $\epsilon/K = 294.6^\circ\text{K}$ for CrO_3 (35) is used, the diffusivity between O_2 and CrO_3 as calculated by the Chapman-Enskog formula (15) gives

$$D_{12} = 1.7613/P_t \quad (\text{cm}^2/\text{sec}) \quad (21)$$

which is approximately 5 times greater than the very low estimate by Graham and Davis (53). The Lennard-Jones force constants for calculating the high temperature binary

diffusion coefficient are given in Table 8.

(2) The model proposed by Graham and Davis (53) is basically a special case of Bartlett's model. After appropriate conversion of units, their model will be the same as Bartlett's model for the special condition of mass transfer control. Bartlett's model representing this reaction system is given by the equation

$$X = \frac{(2\pi M_{\text{CrO}_3} RT)^{-1/2} M_{\text{CrO}_3} K P_{\text{O}_2}^{3/4}}{1 + (2\pi M_{\text{CrO}_3} RT)^{-1/2} P_t / k_m} \quad (22)$$

where X = mass flux of CrO_3 across the boundary layer
($\text{gm-cm}^{-2}\text{-sec}^{-1}$)

R = ideal gas constant = 8.317×10^7
($\text{ergs-mole}^{-1}\text{-}^\circ\text{K}^{-1}$)

P = pressure, 1 atm = 1.0133×10^6 (dyne-cm^{-2})

k_m = mass transfer coefficient ($\text{mole-cm}^{-2}\text{-sec}^{-1}$)

K = equilibrium constant of chromium oxide oxidation reaction.

The mass transfer coefficient k_m can be calculated from equation (20) and (21). The equilibrium constant can be calculated using available data in the literature (84). The viscosity of the gas mixture was calculated from the individual viscosity data using the Herning and Zipperer method (147) in which the gaseous mole fraction and the square root of molecular weight were used as the weighting

Table 8. The Lennard-Jones parameters for calculating the high temperature diffusion coefficient under different reaction systems and the references that have been used for the recalculation.

Reaction system	A	B	σ_{AB} (A)	ϵ_{AB} (K)	Ref.
Oxidation of Cr_2O_3	O_2	CrO_3	3.9665	182.45	27, 53, 59, 87
Chlorination of Cr	Ar	CrCl_3 or CrCl_4	4.06	249	148
Oxid-Chlorination of Cr_2O_3	Ar	CrO_2Cl_2	4.06	249	148
Chlorination of Ni	He	NiCl_2	---1	---1	46
	N_2	NiCl_2	4.191	213.9	65
	Ar	NiCl_2	4.059	249	47
	HCl	NiCl_2	4.0025	424.26	24
Chlorination of Fe	Ar	FeCl_2	4.059	249	47
	HCl	FeCl_2	4.0025	424.26	24

¹Use the formula $D = 3.0(T/970)^{1.65}$ for calculating the diffusion coefficient where 3.0 is the diffusion coefficient at 970°K as reported by Fruehan(46).

factors. The equation is given by

$$u_m = \{\sum y_i u_i (M_i)^{1/2}\} / \{\sum y_i (M_i)^{1/2}\} \quad (23)$$

The comparison between the model prediction and their experimental results is shown in Figure 24. The predicted rates are lower. However, these results are much better than the original comparison (53) based on the boundary layer thickness calculation.

Other experimental studies on this reaction have been carried out by Caplan and Cohen (27), Menzies and Mortimer (104), Hagel (59), Stearns et al. (170) and more recently by Kohl et al. (87). The work done by Menzies and Mortimer (104) is inconsistent with other previous studies and will not be considered here. Caplan and Cohen (27) used cylindrical samples to conduct their experiments at different gaseous environments, including dry oxygen at atmospheric pressure. The reaction temperatures of their study (27) were 1100 and 1200°C. If equation (24) is used to calculate the equivalent spherical diameter of the cylindrical pellet (157) and equation (25) is used to calculate the mass transfer coefficient of a sphere, the values predicted by equation (22) and the experimental results are in good agreement. These are shown in Figure 24.

Figure 24. A comparison between Bartlett's model prediction and the experimental rate data from the literature for the Cr₂O₃ oxidation system.

$$D_p = (D_c X_c + 1/2 D_c^2)^{1/2} \quad (24)$$

where D_p = equivalent sphere diameter

D_c = cylinder diameter

X_c = cylinder length

$$\frac{h_M D_p}{D_{12}} = \frac{k_m D_p}{D_{12}} \frac{RT}{P_t} = 2 + Sc^{1/3} Re^{1/2} \quad (25)$$

In the study of Caplan and Cohen (27), only experimental results were presented and no reaction model was discussed. Bartlett's model presented here provide more insight on their experimental results.

Both Graham and Davis (53) and Caplan and Cohen (27) conducted their experiments under forced convection conditions. The study on the volatilization of Cr_2O_3 in static oxygen at 76 mm Hg atmosphere has been carried out by Hagel (59) between 1175 and 1385°C. Disk samples with diameters equal to 0.75 inch were used. Like many studies, Hagel (59) ran a lot of experiments and made little attempt to develop a reaction model. In order to compare his natural convection experimental results with Bartlett's model, the Chilton-Colburn equation (193, p. 551) relating convective heat and mass transfer is used in this calculation. The Chilton-Colburn equation is given by the equation

$$h_M = \frac{k_m RT}{P_t} = \frac{h_M}{\rho C_p} \left(\frac{C_p \rho D_{12}}{k} \right)^{2/3} \quad (26)$$

where h_M = mass transfer coefficient.

h_H = heat transfer coefficient.

C_p = specific heat of oxygen.

ρ = density of oxygen.

D_{12} = diffusivity.

R = ideal gas constant.

k = thermal conductivity of oxygen.

In keeping with the convention, the values of the properties of gases were determined at film temperatures equal to the average of sample temperature and the ambient free stream temperature. The heat transfer coefficient was determined from the following equation for natural convection with a vertical surface (193, p. 338-340):

$$Nu_L = \frac{h_H L}{k} = 0.678 \left(\frac{Pr}{0.952 + Pr} Gr_L Pr \right)^{1/4} \quad (27)$$

where Nu_L = average Nusselt number over the length L .

$$Pr = \mu C_p / k$$

$$Gr_L = \beta g \rho^2 L^3 \Delta T / \mu^2$$

L = characteristic length which equal to 0.9 times

the diameter of a circular disk (193, p. 338-340).

β = coefficient of thermal expansion.

T = temperature difference between the heated fluid and the bulk value.

The heat capacity of oxygen gas was estimated as (132):

$$C_p = 8.27 + 0.000258 T - 187700/T^2 \quad (\text{cal/mole-deg}) \quad (28)$$

The thermal conductivity k for oxygen can be estimated from the Eucken equation relating the thermal conductivity and the viscosity of a polyatomic gas at low densities (15):

$$k = (C_p + 5/4 R)\mu/M \quad (29)$$

The viscosity at different temperatures was calculated using the empirical equation (119) that takes into account the viscosity collision integrals for the Lennard-Jones (12-6) intermolecular potential. The empirical equation relating the diffusion collision integrals as a function of temperature in the same paper (119) was employed to calculate the diffusion coefficient at different temperatures. These equations are shown as:

$$\Omega_\mu(T, \epsilon_{12}/k) = \frac{A}{T_S^B} + \frac{C}{\text{Exp}(D \cdot T_S)} + \frac{E}{\text{Exp}(F \cdot T_S)} + R \cdot T_S^B \sin(S - T_S^W - P) \quad (30)$$

where ϵ_{12}/K = Lennard-Jones force constant from the empirical combining rules.

$$T_S = T/(\epsilon_{12}/k)$$

$$A = 1.16145, B = 0.14874, C = 0.52487, D = 0.77320$$

$$E = 2.16178, F = 2.43787, R = -6.435 \times 10^{-4},$$

$$S = 18.0323, W = -0.76830, P = 7.27371$$

$$\Omega_D(T, \epsilon_{12}/k) = \frac{A}{T_S^B} + \frac{C}{\text{Exp}(D \cdot T_S)} + \frac{E}{\text{Exp}(F \cdot T_S)} + \frac{G}{\text{Exp}(H \cdot T_S)} \quad (31)$$

where $A = 1.06036, B = 0.15610, C = 0.19300,$
 $D = 0.47635, E = 1.03587, F = 1.52996,$
 $G = 1.76474, H = 3.89411$

Both the viscosity and the diffusion coefficient at high temperatures were estimated using the Chapman-Enskog equation. This information, combined with the equilibrium constant expression for the chromium oxide oxidation reaction, allows for the calculation of a predicted value from Bartlett's model. The equilibrium constant expression according to reference (84) is

$$K = (10^{-24700/T + 6.20})^{1/2} \quad (32)$$

Hagel (59) also reported the following expression to correlate his experimental results on the volatilization rate of chromium oxide.

$$K_v = 0.214 \text{ Exp}(-48800 \pm 3000/RT) \quad (\text{gm/cm}^2\text{-sec}) \quad (33)$$

The results of comparison between the above equation and the model prediction from equation (22) are shown in Figure 24. The good agreement shows that Bartlett's model can predict Hagel's data under natural convection mass transfer with chemical reaction. The same natural convection calculation procedure has been applied to recent target collection experiments conducted by Kohl et al. (87) between 900 and 1100°C at atmospheric pressure. The excellent agreements between the predicted values and their experimental data are also shown in Figure 24.

Stearns et al. (170) studied the oxidative vaporization kinetics of Cr_2O_3 in oxygen from 1000 to 1300°C. One distinct feature of their experimental conditions was the very low total pressure (0.115 torr) as compared with the previous studies (27,53,59,87). Since the Reynold's number range is inapplicable, the mass transfer rate in Stearn's paper (170) cannot be calculated using Fand and Keswani's correlation (39). However, as explained by Stearn et al. (170), the kinetic controlled rate equation which is a special case of Bartlett's model can satisfactorily predict

their experimental result. The results are shown in Figure 24. Other reaction rate at very low pressures (10^{-3} mm Hg) can be found from Hagel's experiment (59) at 1200 and 1375°C. The two experimental results are compared with Bartlett's kinetic controlled model and are shown in Figure 24. In general the low pressure kinetic controlled data are more accurately predictable from Bartlett's kinetic model whereas mass transfer controlled data are not as accurately predictable from mass transfer theory. For those cases under mass transfer control, the surface reaction rates are approximately 10^2 - 10^3 greater than the volatile product diffusion rate. The calculated Sherwood number for the experiment of Graham and Davis (53) is between 0.23 and 2.38, depending on the total pressure and gas flow rate. The corresponding value for the experimental data of Caplan and Cohen (27) is between 2.09 and 2.37. The calculated Nusselt number for natural convection heat transfer is about 1.8 for Hagel's experiment (59) and about 7 for Kohl's experiment (87). The calculated Prandtl number of both Hagel's and Kohl's study is 0.77 whereas the Schmidt numbers are within the range of 0.60 to 0.67. These values are within the validity range ($0.60 < Sc < 2500$ and $0.60 < Pr < 100$) of the Chilton-Colburn analogy equation (193, p. 551) that has been used for predicting mass transfer rates under natural convection conditions. The FORTRAN codes for reevaluation

are shown in Appendix C.

b. Chlorination of chromium

Reinhold and Hauffe

(148) recently studied the corrosion kinetics of Cr at atmospheric pressure between 650 and 800°C by using chlorine and argon gas mixtures. A time-constant weight loss of the specimen sample was observed. This was explained by the volatilization of CrCl_3 and CrCl_4 formed from the reaction of Cl_2 with the scale CrCl_2 and CrCl_3 respectively.

After studying the effect of chlorine gas partial pressure, temperature and flow rate on the reaction rate, Reinhold and Hauffe (148) reported that the diffusion of volatile products across the laminar boundary layer controlled the overall reaction rate. An equation based on the diffusional transport of volatile chlorides through the gaseous boundary layer was proposed. However, no direct comparison between the predicted rate and the experimental rate was given. This is probably due to lack of information to determine the diffusion coefficient of the volatile species.

The more general analysis of the above reaction system with Bartlett's model will lead to the following rate

expression for each equation:

$$R_1 = \frac{(2\pi M_{\text{CrCl}_3} RT)^{-1/2} M_{\text{CrCl}_3} P_{\text{CrCl}_3}}{1 + (2\pi M_{\text{CrCl}_3} RT)^{-1/2} P_t / k_{m1}} \quad (36)$$

$$R_2 = \frac{(2\pi M_{\text{CrCl}_4} RT)^{-1/2} M_{\text{CrCl}_4} K P_{\text{Cl}_2}^{1/2}}{1 + (2\pi M_{\text{CrCl}_4} RT)^{-1/2} P_t / k_{m2}} \quad (37)$$

where R_1 , R_2 = reaction rate of CrCl_2 , CrCl_3 with Cl_2 respectively.

k_{m1} = mass transfer coefficient of CrCl_3 .

k_{m2} = mass transfer coefficient of CrCl_4 .

K = equilibrium constant of CrCl_4 formation reaction.

These model equations are better than the equation proposed by Reinhold and Hauffe (148) in that these equations cover the kinetic controlled region and also allow all of the hydrodynamic variables to be included in the calculation of the mass transfer coefficients k_{m1} and k_{m2} . The equilibrium constant and the vapor pressure are available from the literature (123) as:

$$K = (10^{10.0017-12020/T})^{1/2} \quad (\text{atm}^{1/2}) \quad (38)$$

$$P_{\text{CrCl}_3} = 10^{11.887-11500/T} \quad (\text{mm Hg}) \quad (39)$$

Since the Cl_2 concentration was small compared with the diluent gas Ar in their experiment, it is reasonable to take Ar as the bulk of the gas in the system. The viscosity and diffusion coefficient were recalculated using the Chapman-Enskog equation with the Lennard-Jones parameters of volatile chlorides assumed to be the same as the metal chloride MCl_2 (47). These parameters are given in Table 8. The accurate empirical equation (119) relating the collision integrals as a function of the reduced temperatures (equations 30 and 31) was employed to estimate the transport properties at different reaction temperatures. Since only 2 to 4 cm^2 of coupon surface was given as the dimension of the sample, the length of the sample in the direction of flow was estimated to be 2.0 cm. These informations can be used to estimate the mass transfer coefficient of either CrCl_3 or CrCl_4 from the dimensionless correlation equation (20).

Substitution of all of the available information into the sum of Bartlett's equation will give the predicted rate. Figure 25 shows the comparison between the experimental result and the model prediction. Slightly lower predicted rates are observed. The calculations showed that under all

Figure 25. A comparison between Bartlett's model prediction and the experimental rate data from the literature for the Cr chlorination system.

experimental conditions, R_2 is approximately 10 times greater than R_1 . This is quite consistent with the analysis of Reinhold and Hauffe (148) which showed that the vapor pressure of CrCl_3 can be neglected when compared with the vapor pressure of CrCl_4 below 700°C . Two volatile species are produced under this reaction system. The predictive model can be expected to give good results when the diffusion coefficient of the individual volatile product can be reasonably estimated from species with similar structure and the mass transfer correlation formula is available for the specific sample shape.

c. Oxidation-chlorination of chromium oxide The experimental investigation of the simultaneous attack of Cl_2 and O_2 on Cr_2O_3 has been conducted by Reinhold and Hauffe (148) from 700 to 800°C at atmospheric pressure. The chlorine partial pressure covered the range 10-70 torr and the oxygen partial pressure covered the range 0-200 torr. The diluent gas used was argon. The experimental results indicated that the reaction rate is a linear function of chlorine pressure and the fourth root of oxygen pressure. The overall reaction is given by (148)

Since the rate constant depends on the gas flow rate, the diffusion of CrO_2Cl_2 across the laminar boundary layer

has been assumed to be the rate determining step. Although no experimental data about the flow rate dependence on reaction rate were given, Reinhold and Hauffe (148) proposed the following approximate equation to relate the reaction rate with the experimental variables:

$$\text{Rate} = \text{constant} \times P_{\text{Cl}_2} \times P_{\text{O}_2}^{1/4} \times V_{\infty}^{1/2} \quad (41)$$

where V_{∞} is the linear gas velocity. Since their investigation (148) did not give the explicit meaning of the 'constant' term in the above equation, no direct comparison between the predicted rate and the experimental rate can be made.

However, more quantitative modeling of this reaction can be done through application of Bartlett's model. The assumptions in the recalculation include:

(1) Simplify the complex situation of multicomponent diffusion by assuming that argon is the only major component present in the bulk gas. This allows the binary diffusion theory to be applicable for the diffusion pair CrO_2Cl_2 and Ar.

(2) Make the assumption that CrO_2Cl_2 molecules have the same force constants as the metal chloride MCl_2 (47). This assumption allows the diffusion coefficient of CrO_2Cl_2 -Ar to be predicted from the Chapman-Enskog equation and the empirical combining rules. The Lennard-Jones parameters used

for the calculation are given in Table 8.

(3) The Cr_2O_3 sample pellet diameter of 1.3 cm was used as the characteristic length to calculate the mass transfer coefficient from equation (25).

The equilibrium constant was available in the literature (156) as:

$$K = (10^{-4750/T + 0.86})^{1/2} \quad (\text{atm}^{-1/4}) \quad (42)$$

The same equation relating the collision integrals as a function of the reduced temperature as in the previous cases was used to calculate the diffusivity and the viscosity at high temperatures (119). The viscosity of the gas mixture was calculated from the individual viscosity data using the Herning and Zipperer method (147). These informations can be used for the following model calculation:

$$\text{Rate} = \frac{(2\pi M_{\text{CrO}_2\text{Cl}_2}^{RT})^{-1/2} M_{\text{CrO}_2\text{Cl}_2} K P_{\text{Cl}_2} P_{\text{O}_2}^{1/4}}{1 + (2\pi M_{\text{CrO}_2\text{Cl}_2}^{RT})^{-1/2} P_t / k_m} \quad (43)$$

The comparison between the model calculation and the experimental data is shown in Figure 26. A lower predicted rate than the experimental rate was obtained. Considering the assumptions involved, the agreement between the predictive model and the experimental data can be considered satisfactory. The calculated Reynolds numbers are between

Figure 26. A comparison between Bartlett's model prediction and the experimental rate data from the literature for the Cr₂O₃ oxidation-chlorination system.

1.58 and 2.05 so that the experiments are in the laminar flow region. The calculated Sherwood numbers are around 2.90.

d. Chlorination of nickel The kinetics of high temperature reactions between chlorine gas and the transition metals is important in many metallurgical processes. In most cases the chlorides produced are volatile over a large temperature range, and the reaction continues to proceed on the clean metal surface at all times. Recent work on the chlorination of nickel has been conducted by Fruehan (46) between 890 and 1249°K in Cl_2 -He and Cl_2 -Ar mixture under atmospheric pressure. Different rate controlling steps at different temperature ranges were reported. At the lower temperature range between 890 and 993°K, the transport of NiCl_2 across the boundary layer was found to control the overall reaction rate. The overall reaction is given by

The boundary layer transport equation as proposed by Fruehan (46) is basically a special case of Bartlett's model. Reinterpretation of the data with Bartlett's model is possible using the available data in the literature on the vapor pressure of NiCl_2 (93,158) and from an estimate of the diffusion coefficient. Since the major component of the gas in the bulk is helium, it is reasonable to simplify the multicomponent diffusion by considering the binary diffusion

between He and NiCl_2 as an approximation. Based on the diffusivity value in Fruehan's paper (46) and the power relationship between diffusivity and temperature at high temperatures (15), the diffusion coefficient was estimated from the following expression

$$D_{\text{NiCl}_2\text{-He}} = 3.0 (T/970)^{1.65} \quad (45)$$

where 3.0 is the diffusivity at 970°K as reported by Fruehan (46). The viscosity of the individual gas and its mixture was calculated as in the previous recalculation procedure. The mass transfer coefficient was estimated using equation (20). The standard energy of formation of NiCl_2 is given by (46)

$$\Delta G^0_{\text{NiCl}_2}(\text{g}) = -19840 - 35.91T + 7.97T \log T \quad (\text{cal}) \quad (46)$$

According to this expression, the equilibrium constant around 1000°K is

$$K = \text{Exp}(-\Delta G^0_{\text{NiCl}_2}/RT) = P_{\text{NiCl}_2, \text{s}}/P_{\text{Cl}_2, \text{s}} = 9.88 \times 10^6 \quad (47)$$

where the subscript s means at the solid surface where the reaction occurs. Since $P_{\text{NiCl}_2, \text{s}} \gg P_{\text{Cl}_2, \text{s}}$ at all of Fruehan's experimental conditions, the $P_{\text{Cl}_2, \text{s}}$ term in Bartlett's model can not be replaced by the Cl_2 pressure in the bulk gas as in the study of oxidation/vaporization kinetics of Cr_2O_3 by Graham and Davis (53). In their study

(53), the oxygen pressure in the solid surface was replaced by the corresponding bulk value because of the negligible pressure of the volatile species of CrO_3 on the solid surface. Due to the unknown Cl_2 pressure at the reaction surface, Bartlett's model should be represented by

$$\text{Rate} = \frac{(2\pi M_{\text{NiCl}_2} RT)^{-1/2} M_{\text{NiCl}_2} P_{\text{NiCl}_2, s}}{1 + (2\pi M_{\text{NiCl}_2} RT)^{-1/2} P_t / k_m} \quad (48)$$

The comparison shown in Figure 27 indicates a better prediction by the above equation than the results of Fruehan (46) where a lower predicted rate was obtained. The same calculation procedure has been applied to the experimental data of Hauffe and Hinrichs (65) at 750 and 800°C under atmospheric pressure. The chlorine gas partial pressure covered the range up to 270 torr. The diluent gas used was nitrogen. Linear gas velocities from 5 to 300 cm/min were used in their experiment (65). The experimental results indicated that at fixed temperature and gas velocity, the reaction rate remained constant above a chlorine pressure of 40 torr. This could be explained by the fact that increasing the Cl_2 partial pressure results in decreasing the NiCl_2 diffusion rate in N_2 due to the higher molecular weight of chlorine as compared with nitrogen. Similar phenomena have been reported in Fruehan's investigation (46). Fruehan (46)

Figure 27. A comparison between Bartlett's model prediction and the experimental rate data from the literature for the Ni chlorination system.

found the reaction rate decreased as the chlorine concentration in the Cl_2 -He mixture increased using He as the diluent gas. Hauffe and Hinrichs (65) reported no decrease in the rate when the chlorine partial pressure was increased. This is probably due to the heavier diluent gas N_2 used in their reaction system. Hauffe and Hinrichs (65) presented no kinetic model to predict the reaction rate. In this investigation, the predictions based on Bartlett's model are compared with their experimental results. Table 8 gives the Lennard-Jones parameters used for the recalculation. The results shown in Figure 27 indicate good agreement. The calculated Sherwood numbers are between 0.88 and 2.62 for Fruehan's data, and between 0.30 and 2.31 for the experimental data of Hauffe and Hinrichs. Both cases are under mass transfer control.

McKinley and Shuler (103) studied the kinetics of the heterogeneous reaction of chlorine and nickel between 1200 and 1700°K under low pressures of 0.08 to 0.4 mm Hg. The rate of nickel removal from the surface was found to be first order in chlorine pressure within the above pressure range. No mechanistic model to further interpret the results was given. An attempt to explain their experimental data using the kinetic controlled equation of Bartlett's model was employed in this study. The kinetic controlled model of Bartlett's model is

$$\text{Rate} = (2\pi M_{\text{NiCl}_2} RT)^{-1/2} M_{\text{NiCl}_2} P_{\text{NiCl}_2, s} \quad (49)$$

Since the reaction temperatures of most of their experimental data are between 1395 and 1570°K, it is above the boiling point (1243°K) of NiCl_2 (93) at one atmosphere. Therefore, the $P_{\text{NiCl}_2, s}$ term in the above equation should be replaced by the chlorine pressure in the reaction system in order to obtain the predicted reaction rate. These are compared with the experimental results in Figure 27. Very good agreement is obtained. The model equation also explains the linear relationship between the chlorine pressure and the reaction rate observed by McKinley and Shuler (103).

Fruehan and Martonik (47) studied the chlorination of Ni in HCl-Ar gas mixture between 850 and 1340°K. The overall reaction is given by

and

$$\Delta G^0 = 24725 + 15.13T - 6.15T \log T \quad (\text{cal}) \quad (51)$$

between 800 and 1400°K (47).

At the low temperature range (830°K < T < 980°K) of their experiment, Fruehan and Martonik (47) used the known vapor pressure of NiCl_2 (158) and the mass transfer correlation for flow over a plate to calculate the reaction

rate. However, the rate constant calculated from equation (51) gave $1.3 \times 10^{-6} < K < 1.6 \times 10^{-5}$ between the reaction temperatures. The small K value indicates an insignificant decrease of HCl concentration in the solid surface as compared with the bulk concentration. An approximation can be made so that these two concentrations are equal. Therefore, equation (48) can be changed to the following form for this reaction system.

$$\text{Rate} = \frac{(2\pi M_{\text{NiCl}_2} RT)^{-1/2} M_{\text{NiCl}_2} K^{1/2} P_{\text{HCl}}}{1 + (2\pi M_{\text{NiCl}_2} RT)^{-1/2} P_t / k_m} \quad (52)$$

The above model equation can take into account the change of bulk HCl concentration whereas Fruehan's calculation (47) can not. The same calculation procedure as in previous cases was also used here. The binary diffusion between NiCl_2 and the diluent gas Ar was used as an approximation for mass transfer calculation. The Lennard-Jones parameters for the recalculation are shown in Table 8. The predicted values were obtained by substituting the available information into the above equation. The result shown in Figure 27 indicates a reasonable agreement between the predicted value and the experimental data. The same calculation procedure has also been applied to the earlier study of Brown et al. (24). Brown et al. (24) found

the corrosion rate was roughly proportional to the vapor pressure of NiCl_2 . However, no analysis was given by them. The not very good trend of their data as shown in Figure 27 is probably due to their inappropriate extrapolation of the corrosion rate to longer times and the inaccuracy of the experimental methods used more than 30 years ago. Both studies (24,47) are under the laminar flow region. The calculated Sherwood numbers are around 2.

e. Chlorination of iron The heterogeneous reaction between iron and HCl gas has been studied by Fruehan and Martonik (47) between 808 and 1046°K and by Brown et al. (24) between 620 and 1440°F at one atmosphere. The overall reaction is given by

Fruehan and Martonik (47) found the reaction rate to be controlled by the transport process through the gas film boundary layer at the surface of the sample, and the transport of the volatile product FeCl_2 across the boundary layer control the reaction between 808 and 1046°K. Reinterpretation of the experimental data using Bartlett's model is possible using the available FeCl_2 vapor pressure expression (158), the diffusion coefficient, and the viscosity calculated from the Chapman-Enskog equation. The binary diffusion between FeCl_2 and Ar was used to approximate

the multicomponent diffusion. The Lennard-Jones parameters for recalculation are shown in Table 8. As in the previous case, the empirical collision integrals for the Lennard-Jones potential (119) were used to calculate the transport properties at different temperatures. The gas mixture viscosity was estimated from individual viscosity using the Herning and Zipperer method (147). The mass transfer rates were calculated using equation (20) for the strip sample. The model equation is represented by

$$\text{Rate} = \frac{(2\pi M_{\text{FeCl}_2} RT)^{-1/2} M_{\text{FeCl}_2} P_{\text{FeCl}_2}}{1 + (2\pi M_{\text{FeCl}_2} RT)^{-1/2} P_t/k_m} \quad (54)$$

The comparison between the predicted values from the above equation and the experimental values from both studies (24,47) are shown in Figure 28. Reasonably good agreement can be found from them. The calculated Sherwood numbers are around 2 and the surface reaction rates are approximately 10^4 greater than the diffusion rates under these particular experimental conditions.

2. Comparison of the results of this work with other related studies and the mass transfer predictions

Although the volatilization of pure Cr_2O_3 at high temperatures under an oxidation atmosphere is widely

Figure 28. A comparison between Bartlett's model prediction and the experimental rate data from the literature for the Fe chlorination system.

recognized and the kinetics of this reaction can be characterized by the previously discussed Bartlett's model, the volatilization data from the commercial alloys forming the protective Cr_2O_3 scale are not widely reported and discussed. Several experimental volatilization data available in the literature can be found from the work of Lewis (97), Davis et al. (32), Croll and Wallwork (30) and Barrett and Lowell (9). All of these experiments used alloys that formed a continuous Cr_2O_3 layer as a means to prevent high temperature corrosion reaction. Their volatilization rates, derived from fitting the thermogravimetric results to different kinetic model in the individual study, were compared with the present work on the Armco 18SR-A, 18SR-B, 18SR-C and T310 alloy. The gas mixture used in the present study is SO_2/O_2 . Cr_2O_3 is the thermodynamically stable condensed phase. The derivation of the volatilization rate for the present work has been discussed in section (IV-B). Figure 29 shows the comparison at different temperatures. Also shown in Figure 29 are the results of Hagel (59) on the oxidation of chromium oxide at a static oxygen under 0.1 atmosphere. The following equation was reported by Hagel to correlate his experimental results from 1175 to 1385°C (59)

$$K_v = 0.214 \text{ Exp}(-48800 \pm 3000/RT) \quad (\text{gm/cm}^2\text{-sec}) \quad (33)$$

where K_v is the vaporization rate. It is noted that the

Figure 29. Experimental volatilization rate of the alloys forming Cr₂O₃ protective layer are compared with Hagel's correlation.

above equation has been extrapolated to the lower temperature region in Figure 29. However, the uncertainty limit of this equation still covers most of the available experimental results.

The temperature dependence of the volatilization rate for this study is shown in Figure 30 for Armco 18SR alloys. Although all of the samples have the same chemical composition, sample A always has the higher volatilization rate compared to samples B and C. The effect of heat treatment on the volatilization rate is clearly demonstrated in these results. However, the basic mechanism is not yet understood. The volatilization rates from this work were fitted to the Arrhenius equation

$$K_v = 1.336 \times 10^{-4} \text{ Exp}(-29286 \pm 5801/RT) \quad (\text{gm/cm}^2\text{-sec}) \quad (55)$$

The R^2 statistic is 0.7845. The activation energy of this study, 29286 cal/mole, is within the range of the results of Lewis' study (97) which ranged from 18000 to 53000 cal/mole.

The experimental volatilization rate of the present study and the above mentioned investigations (9,30,32,97) have also been compared with the high temperature mass transfer predictions. All of these runs are under the pressure region where the transport of the volatile product CrO_3 across the gaseous boundary film control the reaction rate. Therefore no surface reaction rate calculations are

Figure 30. Temperature dependence of the volatilization rate of Armco 18SR. The 95% confidence interval of each experimental point is given by the error bars.

needed. The experimental conditions of the present study have been given in the previous section. The reaction temperatures used were 900, 1000 and 1100°C where the volatilization rate becomes significant. The equilibrium gas composition in the reaction column can be calculated (Appendix B) using the stoichiometric relationships between the reaction species and the available expression for the Gibbs energy of formation. The calculated equilibrium mole fraction of gaseous species in the reaction column was used to calculate the heat capacity and the thermal conductivity of the gas mixture from the individual property. The binary diffusion between CrO_3 and oxygen was used to approximate the multicomponent diffusion. The experimental conditions of the other related studies (9,30,32,97) are given in Table 9. Equation (56) and (57) from reference (77) were used to calculate the Nusselt number taking into account the cylindrical shape of the sample in Lewis' study (97). The Chilton-Colburn analogy given by equation (26) was used to calculate the mass transfer rate.

$$\text{Nu} = 0.138 \text{Gr}^{0.36} (\text{Pr}^{0.175} - 0.55) \quad \text{for } \text{Gr} > 10^9 \quad (56)$$

$$\text{Nu} = 0.683 \text{Gr}^{0.25} \text{Pr}^{0.25} \{ \text{Pr} / (0.861 + \text{Pr}) \}^{0.25} \quad \text{for } \text{Gr} < 10^9 \quad (57)$$

The procedure of calculating the mass transfer rate for Hagel's data discussed in section (V-B-1-a) was used to

Table 9. Experimental conditions of related studies and the equations for predicting mass transfer rates.

	Davis et al. (32)	Croll & Wallwork (30)	Lewis (97)	Barrett & Lowell (9)
Temperature	1200°C	1000°C	800-1200°C	1150°C
Gas flow	forced convection $V=12$ cm/s	natural convection	natural convection	natural convection
Pressure	$P_{\text{tot}}=P_{\text{O}_2}$ (150 torr)	$P_{\text{tot}}=P_{\text{O}_2}$ (200 torr)	air (1 atm.)	air (1 atm.)
Sample	square $A=1 \times 1$ $\times 2$ cm ²	rectangle $A=1 \times 1.5$ $\times 2$ cm ²	cylinder dia.=1.3 cm $L=1.9$ cm	rectangle $A=1.27 \times 1.9$ $\times 2$ cm ²
Eq. no. for mass transfer calculations	20	26, 27	26, 56, 57	26, 27

predict the mass transfer rate for the data of Croll and Wallwork (30), Lewis (97), Barrett and Lowell (9) and this work. In all cases, the experiments were under natural convection conditions. The procedure of calculating mass transfer rate for Graham's data discussed in section (V-B-1-a) was followed to predict the mass transfer rate for the study of Davis et al. (32) where forced convection condition prevail. The diffusion coefficient of CrO_3 was calculated from the Chapman-Enskog equation using the Lennard-Jones (12-6) potential and the empirical combining rules. The comparison between the predicted mass transfer rate and the experimental rate is shown in Figure 31. The lower predicted mass transfer rate is probably due to the inaccuracy in the determination of the high temperature diffusion coefficient from the Chapman-Enskog equation using the Lennard-Jones force constants derived from the low temperature viscosity measurement. This will be further examined in the next section.

3. Effect of high temperature on the prediction of gaseous diffusion coefficient

The prediction of the gaseous diffusion coefficient is essential for calculating the gas-solid mass transfer rate either under natural convection or under forced convection conditions. The frequently used experimental method for

Figure 31. A comparison between the experimental volatilization rate of the alloys forming Cr₂O₃ layer and the predicted volatilization rate from mass transfer calculations.

determining the diffusion coefficient has been reviewed by Marrero and Mason (101) and Westenberg (195). Generally the temperature dependence of the diffusion coefficient varies for different temperature ranges. The qualitative dependency has been graphically shown by Reid et al. (146) and Marrero and Mason (101). The correlation that the diffusion coefficient increases roughly as the 2.0 power of T at low temperatures and as the 1.65 power of T at very high temperature (15) has also been confirmed by many experimental results. Normally the diffusion coefficient at ordinary temperatures is easier to determine than at higher temperatures especially for the common static method. Because of the limited data available for the high temperature diffusion coefficient, different predictive and experimental methods have evolved during the past years. Generally, these methods can be classified into four categories: (1) molecular beam scattering experiments; (2) other transport properties, such as viscosity, at high temperatures; (3) calculations based on the extended principle of corresponding states and; (4) calculations based on the Chapman-Enskog equation using the Lennard-Jones (12-6) potential and the empirical combining rules.

The method based on the molecular beam scattering experiment was first developed by Amdur (2). As a result of the extremely complex nature of the molecular scattering

experiment, the current available data from this method have been confined to a limited number of compounds, such as the rare gases and nitrogen containing gases. The experimental results are generally correlated using the inverse power potential or the exponential power potential which is the most reliable empirical function that takes into account the important short range repulsion force between molecules at high temperatures. The good agreement between the scattering experiments for several diffusion systems (187,188) give good evidence of the validity of predicting high temperature transport properties from scattering potential and rigorous kinetic theory.

Prediction of the high temperature diffusion coefficient from the other transport properties, especially from high temperature viscosity data has proven to be very accurate (3,34,45,71,76,78,79,83,112,171,191,192). This procedure is virtually independent of the molecular interactions, and hence the assumed potential function. Since the measurement of viscosity is much more accurate than the measurement of diffusion coefficient, it provides a method for obtaining the diffusion coefficient under conditions where direct diffusion measurements are difficult to make, especially at high temperatures.

In order to calculate the diffusion coefficient based on the statistical mechanical theory, the intermolecular

potential function is needed. In addition to the molecular scattering method, the potential of intermolecular forces between molecules may be derived by a priori calculations based on solutions of the Schroedinger equations or from macroscopic measurement with the aid of statistical mechanical theory (4). However, due to the complexity of the first two methods, the third method has been used extensively. Usually the equilibrium or non-equilibrium property is determined experimentally as a function of temperature and an analytical form is assumed for the intermolecular potential. The determination of the unknown parameters in the potential function is based on statistical mechanical theory and least square principles that minimize the sum of square residuals between the experimental data and the prediction based on the kinetic theory. However, many previous investigations indicated that none of the proposed intermolecular potential with its parameters derived from one kind of macroscopic property by the curve fitting method can correlate several other properties of a single gas or many gases with good accuracy. Even if such curve fitting procedures were crowned with success, it would be rash to assume that the 'true' potential functions have been discovered (82). Unifying the properties of gases with the principle of corresponding state is based on the assumption that the gases considered obey the same intermolecular

potential function and differ from each other merely in the numerical values of the parameters which are the scaling factors. Therefore, a number of empirically determined universal functions based on the existing data must replace the corresponding integrals of the Chapman - Enskog equation. Studies in this field can be found from many references (23,67,78,79,80,81,82,102). The maximum utilization of theory and experimental data is carried out with this procedure.

Although the exponential repulsion potential or the exp-6 potential was considered to be better for correlating the high temperature transport data, there are many studies correlating the high temperature results using the Lennard-Jones (12-6) potential (13,36,37,38,124,125,160,162,187,189,194,195,196). From an engineering point of view, it is more convenient to use a single potential function of the widest possible applicability. For calculating from kinetic equation describing the gaseous diffusion coefficient, the Lennard-Jones (12-6) potential appears to be the most generally used of many potential functions which have been proposed. This is especially true in the high temperature gas - solid reactions with formation of volatile species in which the transport process within the gaseous boundary layer is a very important factor. Many investigations in this field predicted the high temperature diffusion coefficient

with the Chapman-Enskog equation using the Lennard-Jones force constants from the low temperature viscosity measurements (10,11,35,46,47,53,63,190), or predicted the high temperature diffusion coefficient from the Wilke-Lee modification of the Hirschfelder-Bird-Spotz equation (197,198). A careful analysis of their results indicated that only the oxidation of tungsten (10,190) and the oxidation of iridium (197,198) gave good predictive results. The oxidation of the iridium system will certainly give good results since their experimental data (197,198) were correlated with their model equation and the other unknown properties found from this procedure. With the above exceptions, all of the other systems (11,35,46,47,53,63) gave a lower predicted value than the experimental data. None of the above investigations attempted to explain this discrepancy except the work done by Fruehan and his coworker (46,47) who proposed that the inaccuracy of the mass transfer dimensionless correlation equation was responsible for the error. However, from the discussions in section (V-B-1) and (V-B-2) it can be shown that many recent results show a lower predictive value if the data are in the mass transfer controlled region and if the high temperature diffusion coefficients are evaluated from the Chapman-Enskog equation using the Lennard-Jones (12-6) parameters from the low temperature viscosity measurement or from similar molecules.

The agreements between the model prediction and the literature data are generally better if kinetic control prevailed so that no calculation of high temperature diffusion coefficient is needed (section V-B-1). The availability of many reliable high temperature diffusion data at around 1000°K from the literature makes it possible to compare the prediction based on the above mentioned calculational method. The results are given in Table 10 for the self-diffusion part and the binary diffusion part. It was found that for noble gases, the average relative error between the reliable sources and the calculations is about 3% under the self-diffusion category and about 7% under the binary diffusion category. The larger error in the latter is probably due to the application of the empirical combining rules and the effect of neglecting the second approximation in the Chapman-Enskog equation. For the other gaseous pairs, the predicted values are approximately 15% lower than the reliable high temperature diffusion data. As the temperature is increased above 1000°K, the deviation from the experimental value increases.

From above discussions, it is found that most of the high temperature diffusion coefficients were predicted using the Chapman-Enskog equation with the Lennard-Jones force constants derived from the low temperature viscosity measurement. As a result, the predicted volatilization rates

Table 10. Comparison between the reliable diffusion coefficient around 1000°K under atmospheric pressure and the calculation from the Chapman - Enskog equation using the Lennard-Jones (12-6) parameter from viscosity measurement and empirical combining rules.

Gas Pair	T(K)	Literature Value (cm ² /s)	Calc. Value	error (%) ¹	Ref.
A. Self-diffusion part:					
He-He	1000	13.3 ²	12.11	8.9	3
³ He- ⁴ He	888.3	11.8 ³	10.97	7.0	34
	888.3	11.4 ⁴	10.97	3.8	34
	888.3	11.4 ⁵	10.97	3.8	34
Ne-Ne	1000	3.93 ²	3.77	4.1	3
	1000	3.92 ⁶	3.77	3.8	112
Ar-Ar	1000	1.51 ²	1.46	3.3	3
	1000	1.50 ⁶	1.46	2.7	112
	1000	1.66 ⁷	1.46	12.0	2
	1000	1.48 ⁸	1.46	1.4	2
Kr-Kr	1000	0.853 ²	0.86	-0.8	3
	1000	0.846 ⁶	0.86	-1.7	112
	1036.1	0.934 ³	0.913	2.2	191
	1036.1	0.923 ⁴	0.913	1.1	191
	1036.1	0.933 ⁵	0.913	2.1	191

¹(literature value - calc. value)/literature value.

²From viscosity which in turn from the combined potential function.

³Two bulb method.

⁴From high temperature viscosity data.

⁵From high temperature thermal conductivity data.

⁶From high temperature conductivity data and kinetic theory using 11-6-8 potential.

⁷10⁴ρD₁₁=7.1 gm/cm-sec from the Lennard-Jones parameters by low temperature Ar viscosity measurement; the corresponding value from the potential derived from molecular beam scattering experiment is 8.1 gm/cm-sec.

⁸Best smoothed value of 10⁴ρD₁₁=7.2 gm/cm-sec.

Table 10 (continued)

Gas Pair	T (K)	Literature Value (cm ² /s)	Calc. Value	error (%) ¹	Ref.
Xe-Xe	1000	0.502 ²	0.51	-1.6	3
N ₂ -N ₂	1000	1.56 ²	1.56	0.0	3
	1000	1.61 ⁹	1.56	3.1	2
	1000	1.52 ¹⁰	1.56	-2.6	2
CO ₂ -CO ₂	1103	1.63 ¹¹	1.11	31.9	124
	1180	1.84 ¹¹	1.268	31.1	37
	1200	1.84 ¹¹	1.33	27.7	38

B. Binary diffusion part:

He-Ar	993.15	5.647 ^{4,12}	5.38	4.7	76
	1000	5.824 ¹³	5.44	6.6	171
	1000	6.23 ¹⁴	5.44	12.7	195
	1142	7.00 ¹⁵	6.78	3.1	160
He-Kr	993.15	4.836 ^{4,12}	4.88	-0.9	76
	1000	5.746 ¹³	4.94	13.2	171
He-Xe	778	2.675 ⁴	2.675	0.0	79
	1000	4.869 ¹³	4.11	15.6	171
Ne-Ar	973.15	2.381 ⁴	2.265	4.9	83
Ar-Kr	973.15	1.156 ⁴	1.109	4.1	83

⁹Like 7 except the corresponding values are 5.4 and 5.5.

¹⁰Best smoothed value of $10^4 \rho D_{11} = 5.2$ gm/cm-sec.

¹¹Modified point source technique.

¹²Equimolar composition.

¹³Ave. D_{12} from η_{mix} .

¹⁴Average value of I-J, M.B, IPR and Exp R potentials; point source technique.

¹⁵Diffusion bridge (porous septum).

Table 10. (continued)

Gas Pair	T(K)	Literature Value (cm ² /s)	Calc. Value	error (%) ¹	Ref.
Kr-Xe	1000	0.7403 ¹³	0.67	9.5	171
He-N ₂	882	4.204 ¹⁵	4.234	-0.7	36
	1000	5.67 ¹⁴	5.34	5.8	195
H ₂ -Ar	1000	7.23 ¹⁴	6.25	13.6	195
CO ₂ -Ar	1181	1.88 ¹¹	1.54	18.1	125
CO ₂ -N ₂	880	1.050 ¹⁵	0.99	5.7	36
	1000	1.46 ¹⁴	1.24	15.0	195
	1000	1.50 ¹⁶	1.24	17.3	71
	1000	1.45 ¹¹	1.24	14.5	45
	1081	1.64 ¹¹	1.41	14.0	125
	1107	1.68 ¹⁵	1.47	12.5	160
CO ₂ -O ₂	1000	1.43 ¹⁴	1.24	13.3	195
CO-O ₂	1000	1.75 ¹⁴	1.63	6.9	195
CH ₄ -O ₂	1000	1.98 ¹⁴	1.79	9.6	195
H ₂ -O ₂	1000	7.02 ¹⁴	6.07	13.5	195
H ₂ O-O ₂	1000	2.21 ¹⁴	2.08	5.9	195
CO ₂ -H ₂ O	1000	2.08	1.58 ¹⁷	24.0	38
H ₂ -N ₂	1016	5.79 ¹⁵	5.90	-1.9	160
H ₂ -CO ₂	989	5.76 ¹⁵	4.80	16.7	160

¹⁶From thermal diffusion calculations.

¹⁷CO₂ parameters derived from high temperature viscosity data;
H₂O parameters derived from the 2nd virial coefficient.

under mass transfer controlled conditions are lower than the results from literature and the present investigation.

VI. CONCLUSIONS

The use of thermogravimetric technique for the study of high temperature corrosion kinetics under SO_2/O_2 atmosphere has been applied to Armco 18SR alloys that have different heat treatment histories, Armco T310 alloy and pure chromium samples between 750 and 1100°C. The weight changes of the alloy samples follow the parabolic rate law. The volatilization of the protective Cr_2O_3 layer was taken into account above 900°C and where the experiments were run for long periods of time. The experimental parabolic rate constant and the volatilization rate constant were calculated from the data using the modified Tedmon's model. Both rate constants were solved simultaneously from the modified Tedmon's kinetic equation by non-linear regression. The following are the main conclusions from the experimental part of this investigation:

(1) Although the Armco 18SR alloys have the same chemical composition but different heat treatment histories, the Armco 18SR-C sample has the best resistance to corrosion of the three alloys tested in this investigation. It formed a compact and adherent scale. Armco 18SR-C alloy also gives the lowest volatilization rate in comparison with 18SR-A and 18SR-B. Increasing the gas flow rate and SO_2/O_2 ratio showed no significant effect on the parabolic and volatilization rate of 18SR-C under the present experimental conditions.

Armco 18SR-A is the least corrosion resistant of the Armco 18SR alloys. It has the highest parabolic and volatilization rate of the three Armco 18SR alloys and its scale flakes off on cooling. The apparent activation energy using the parabolic rate constant is 28727 cal/mole for 18SR-A compared with 78412 cal/mole for 18SR-B and 18SR-C.

(2) Armco T310 alloy usually gives good resistance to SO_2/C_2 atmosphere at temperatures around 800°C but gives a very high corrosion rate at 1000-1100°C. The formation of a mixture of Cr_2O_3 , gamma- Fe_2O_3 and NiO in the early stage of the reaction and the subsequent formation of the sulfide phase by sulfur penetration contribute to the high corrosion rate at high temperatures. The apparent activation energy using the parabolic rate constant is 43028 cal/mole for Armco T310 alloy.

(3) Very little work has previously been reported on pure chromium in SO_2/O_2 atmosphere. In general the chromium sample is not protective under SO_2/O_2 atmosphere. Small amounts of oxide and sulfide inclusions were found below 820°C where an apparent continuous oxide scale was developed. A continuous sulfide layer near the surface leads to the enhanced corrosion rate above 900°C. This is attributed to the penetration of the sulfur bearing species through the pores or cracks of the outer oxide layer to a low oxygen activity site where the sulfide formation is

thermodynamically favorable. The parabolic rate constant in the short term runs are comparable with the literature results under pure oxidation condition. The apparent activation energy using the parabolic rate constant is in very good agreement to the previous investigations under pure oxidation conditions.

The kinetics of gas-solid reaction with volatilization of the reaction product have only been investigated to a limited extent. This has been done in the present investigation by examining the available experimental data in the literature and by conducting the experiments using iron based alloys forming Cr_2O_3 protective scales. The parabolic kinetic behavior of the alloy in the present investigation was analyzed using the modified Tedmon's model so that the volatilization loss of Cr_2O_3 via CrO_3 formation can be calculated. The conclusions from this part of the investigation are:

(1) The available rate data on the oxidation of chromium oxide, chlorination of chromium, oxidation-chlorination of chromium oxide, chlorination of nickel and chlorination of iron have been found to be predictable using Bartlett's model. Both product transport control and surface reaction control conditions have been found for the oxidation of chromium oxide and the chlorination of nickel system. For systems under mass

transfer control, the surface reaction rate was found to be 10^2 - 10^4 greater than the mass transfer rate. The flow conditions of the reported reaction rate in the literature include both forced convection and natural convection condition. As long as the gas transport properties can be reasonably estimated and the correlation equation for calculating the mass transfer coefficient is available, good prediction can be expected.

(2) Hagel's correlation on the volatilization rate of pure Cr_2O_3 between 1175 and 1385°C was found to cover most of the experimental volatilization rate from different alloys forming Cr_2O_3 scale. These include the available data in the literature and the present study at temperatures below 1100°C.

(3) The apparent activation energy using the volatilization rate from Armco 18SR alloys is 29286 cal/mole. The other related activation energy reported in the literature for the alloy system is very limited. Only Lewis (97) reported that values ranged from 18000 to 53000 cal/mole for the nickel-chromium alloys under oxidation conditions.

(4) The volatilization rates in the present experimental study and those in the literature for different alloy systems were compared with the mass transfer predictions. Lower predicted rates than the experimental rates were observed. This is due to the estimation of the

high temperature gaseous diffusion coefficient from the Chapman-Enskog equation which uses the Lennard-Jones (12-6) parameters derived from low temperature viscosity measurements. A review of the available rate data in the literature on gas-solid reactions with volatilization of product under mass transfer controlled conditions, and a comparison between the reliable high temperature diffusion coefficient around 1000°K have indicated that the predicted diffusion rate is almost always lower than the experimental rate at high temperatures.

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VIII. APPENDIX A:

SAS PROGRAM FOR CALCULATING THE RATE
CONSTANTS FROM DIFFERENT KINETIC MODELS

```

1      DATA YL1; FACTOR=2.469/10.0**4;
2      AREA=27.65;
3      INPUT T WT; WPA=WT*FACTOR/AREA; TSQRT=SQRT(T*3600); TSEC=-T*3600;
4      W=WPA*100**2;
5      KEEP T WT WPA TSQRT TSEC W; CARDS;

```

NOTE: DATA SET WORK.YL1 HAS 29 OBSERVATIONS AND 6 VARIABLES. 250 OBS/TRK.
 NOTE: THE DATA STATEMENT USED 0.13 SECONDS AND 104K.

```

35      PROC PRINT; TITLE EXPERIMENTAL DATA FOR RUN;

```

NOTE: THE PROCEDURE PRINT USED 0.17 SECONDS AND 104K AND PRINTED PAGE 1.

```

36      PROC PLOT; PLOT WT*T='*' / HPOS=60 VPOS=40;
37      PLOT WPA*T='*' / HPOS=60 VPOS=40;
38      LABEL WPA=WT. GAIN PER AREA(GM/CM**2) T=TIME(HOUR);
39      * MODIFIED TEDMON'S NON-LINEAR MODEL;

```

NOTE: THE PROCEDURE PLOT USED 0.23 SECONDS AND 124K AND PRINTED PAGES 2 TO 3.

```

40      PROC NLIN ITER=200;
41      PARAMETERS KP=0.1,0.2 KS=0.005,0.01,0.05;
42      BOUNDS KP>0 KS>0; A=-KS/KP*W-LOG(1-KS/KP*W); MODEL T=KP/KS**2*A;
43      DER.KP=1/KS**2*A+KP/KS**2*(KS/KP**2*W-(KS*W/KP**2)/(1-KS*W/KP));
44      DER.KS=-2*KP/KS**3*A+KP/KS**2*(-W/KP+(W/KP)/(1-KS*W/KP));
45      TITLE MODEL 1. D(W/A)/DT=KP/(W/A)-KV;
46      * NO INTERCEPT MODEL W/A=BETA1*SQRT(T)-BETA2*T;

```

NOTE: THE PROCEDURE NLIN USED 0.80 SECONDS AND 148K AND PRINTED PAGES 4 TO 6.

```

47      PROC MATRIX; FETCH RXR DATA=YL1; NR=NROW(RXR);
48      A= 0 / 0 / 1 / 0 / 0 / 0;          B= 0 / 0 / 0 / 1 / 0 / 0;
49      C= 0 / 0 / 0 / 0 / 1 / 0;          E=B||C;
50      Y=RXR*A; X=RXR*E; D=INV(X*X); BETA=D*X*Y; YHAT=X*BETA; RESID=Y-YHAT;

```

```

51      SSERROR=RESID*RESID; SSTOTAL=Y*Y; SSREG=SSTOTAL-SSERROR;
52      RSQUARE=SSREG#/SSTOTAL; MSERROR=SSERROR#/(NR-1); F=SSREG#/MSERROR;
53      P1= 0 / 1; P2= 1 / 0; P3=ROWSSQ(BETA); BETA=BETA#P1+P3#P2;
54      SD=(DIAG(D)#SSERROR)##(0.5);
55      PRINT BETA SD SSREG SSERROR SSTOTAL RSQUARE F;
56      TITLE MODEL II. W/A=BETA1*SQRT(T)-BETA2*T;
57      * WITH INTERCEPT MODEL W/A=BETA1*SQRT(T)-BETA2*T+BETA3;

```

NOTE: THE PROCEDURE MATRIX USED 0.21 SECONDS AND 130K AND PRINTED PAGE 7.

```

58      PROC MATRIX; FETCH RXR DATA=YL1; NR=NROW(RXR);
59      A= 0 / 0 / 1 / 0 / 0 / 0;          B= 0 / 0 / 0 / 1 / 0 / 0;
60      C= 0 / 0 / 0 / 0 / 1 / 0;          E=B||C;
61      Y=RXR*A; XX=RXR*E; X=XX||J(NR,1);
62      D=INV(X*X); BETA=D*X*Y; YHAT=X*BETA; RESID=Y-YHAT;
63      SSERROR=RESID*RESID; SSTOTAL=Y*Y; SSREG=SSTOTAL-SSERROR;
64      RSQUARE=SSREG#/SSTOTAL; MSERROR=SSERROR#/(NR-1); F=SSREG#/MSERROR;
65      P1= 0 / 1 / 1; P2= 1 / 0 / 0; P3=ROWSSQ(BETA); BETA=BETA#P1+P3#P2;
66      SD=(DIAG(D)#SSERROR)##(0.5);
67      PRINT BETA SD SSREG SSERROR SSTOTAL RSQUARE F;
68      TITLE MODEL III. W/A=BETA1*SQRT(T)-BETA2*T+BETA3;

```

NOTE: THE PROCEDURE MATRIX USED 0.23 SECONDS AND 130K AND PRINTED PAGE 8.

NOTE: SAS USED 148K MEMORY.

IX. APPENDIX B:

CALCULATION OF THE EQUILIBRIUM COMPOSITION

The following standard free energy of reactions for reactions (1) and (2) were obtained from Kubaschewski et al. (93) .

Addition of these two equations give:

for the temperature range 298-1800°K. Assume the incoming volume ratio (or mole ratio) of $\text{SO}_2/\text{O}_2=r$. If the equilibrium conversion of O_2 by equation (3) is x and the equilibrium production of S_2 by equation (1) is y , then the equilibrium number of moles will be

$$\text{SO}_2 : r - 2x - 2y$$

$$\text{O}_2 : 1 - x + 2y$$

$$\text{SO}_3 : 2x$$

$$\text{S}_2 : y$$

The total number of moles is equal to $r-x+y+1$. The partial pressures of the gases at a total pressure of 1

atmosphere are:

$$P_{SO_2} = \frac{r-2x-2y}{r-x+y+1} \quad (4), \quad P_{SO_3} = \frac{2x}{r-x+y+1} \quad (6)$$

$$P_{O_2} = \frac{1-x+2y}{r-x+y+1} \quad (5), \quad P_{S_2} = \frac{y}{r-x+y+1} \quad (7)$$

These partial pressures are related to the equilibrium constant by:

$$K_1 = \text{Exp}(-\Delta G_1^0/RT) = \frac{P_{S_2} P_{O_2}^2}{P_{SO_2}^2} = \frac{y(1-x+2y)^2}{(r-x+y+1)(r-2x-2y)^2} \quad (8)$$

$$K_2 = \text{Exp}(-\Delta G_3^0/RT) = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{4x^2(r-x+y+1)}{(r-2x-2y)^2(1-x+2y)} \quad (9)$$

The x and y values can be calculated from equation (8) and (9) if T and r are specified in these equations. However, since P_{S_2} will be very small as compared with the pressure of the other species, an approximation can be employed so that $y = 0$ at the temperature of interest. Under this approximation, equation (4) to equation (9) can be changed to:

$$P_{SO_2} = \frac{r-2x}{r+1-x} \quad (10)$$

$$P_{O_2} = \frac{1-x}{r+1-x} \quad (11)$$

$$P_{SO_3} = \frac{2x}{r+1-x} \quad (12)$$

$$K_3 = \text{Exp}\left(\frac{45200-42.72T}{1.987T}\right) = \frac{4x^2(r+1-x)}{(r-2x)^2(1-x)} \quad (13)$$

For every selected T and r, x can be calculated from equation (13) by using the interval halving method (51) with a FORTRAN computer program. For each set of variables the iteration is terminated when the difference between the left hand side and the right hand side of equation (13) is less than 10^{-5} . The calculated P_{SO_2} and P_{O_2} can be substituted into equation (8) to find P_{S_2} . The calculated range covered temperatures from 700-1200°C and $1 < r < 12$ for a total pressure of 1 atmosphere. The calculated values in this work are in agreement with previously published results (182).

X. APPENDIX C:

TYPICAL FORTRAN PROGRAM FOR RECALCULATING
THE PREVIOUSLY REPORTED EXPERIMENTAL DATA

```

      SJC8          LIU,PAGES=50
1      REAL K1,K1C,MUMIX,NUMIX,NSC,NRE,KM,KEQ,NSH
2      REAL MCR,MCR03
3      REAL NU,KGI,L
4      DIMENSION PT(36),X(36),V(36),K1(36),K1C(36),AK1(36),AK1C(36)
5      DIMENSION TEMP(10),TIME(10),FLO(10),WL(10),RE(10),RC(10)
6      DIMENSION TE(15),PG2(15),RR(15),RP(15)
7      DIMENSION RR1(6),RP1(6),PTOTAL(7)
8      DIMENSION RR2(12),RP2(12)
9      A=1./((2.*3.14159*100.*8.317*10.**7*(1200+273))**.5)
10     KEQ=SQRT(30.0/(10.0**12))
11     WRITE(6,1)
12     1 FORMAT(1H1, 1X,'EXPERIMENTAL CONDITION AND OBSERVED RATE FOR GRAHA
      3M DATA:',
      1//5X,'NO.',3X,'TOT. PRESSURE',6X,'OXYGEN MOLE FR.',5X,
      2'GAS VELOCITY',6X,'OBSERVED RATE'//)
13     DO 10 I=1,31
14     READ(5,5) PT(I),X(I),V(I),K1(I)
15     5 FORMAT(3F10.4,E10.1)
16     WRITE(6,6) I,PT(I),X(I),V(I),K1(I)
17     6 FORMAT(17,F15.3,F17.4,F21.3,E18.3)
18     10 CONTINUE
19     WRITE(6,15)
20     15 FORMAT(1H1, 5X,'NO.',4X,'SCHMIDT NO.',4X,'REYNOLD NO.',
      14X,'SHERWD. NO.',4X,'RX./MASS TRANS.',4X,'MASS TRANS. RATE',
      24X,'OBSERVED RATE',5X,'CAL. RATE'///)
21     DO 25 I=1,31
22     D12=1.7613/PT(I)
23     MUMIX=(4.330*0.001-8.51*0.0001*X(I))/(6.32-0.66*X(I))
24     RHOMIX=8.274*PT(I)*(32.*X(I)+39.95*(1.-X(I)))/10.**6
25     NUMIX=MUMIX/RHOMIX
26     NSC=NUMIX/D12
27     NRE=V(I)/NUMIX*1.0
28     NSH=0.664*NSC**(1./3.)*NRE**(1./2.)
29     FACTOR=RHOMIX/(32.*X(I)+39.95*(1.-X(I)))
30     KM=D12*NSH*FACTOR
31     AA=A*100.*KEQ*(PT(I)*X(I)*1.0133*10.**6)**(0.75)*(1.0133*10.**6)**
      1 (.25)

```

```

32      BB=A*(PT(I)*1.0133*10.**6)/KM
33      K1C(I)=AA/(1.0+BB)
34      K1(I)=K1(I)*2.*100./152.
35      WRITE(6,20) I,NSC,NRE,NSH,BB,KM,K1(I),K1C(I)
36      20 FORMAT(I8,F14.2,F15.2,F17.2,F19.2,E16.2,E19.2,E16.2/)
37      K1(I)=ALOG10(K1(I))
38      K1C(I)=ALOG10(K1C(I))
39      25 CONTINUE
40      WRITE(6,1001)
41      1001 FORMAT(1H1,1X,'EXPERIMENTAL CONDITION AND OBSERVED RATE FOR CAPLAN
      1 DATA:',
      2//4X,'NO.',9X,'TEMP(C)',8X,'TIME(HR.)',5X,'FLOW(CC/MIN.)',5X,'WL(M
      3G.)'//)
42      DO 1000 I=1,9
43      READ(5,100) TEMP(I),TIME(I),FLO(I),WL(I)
44      100 FORMAT(4F10.1)
45      WRITE(6,101) I,TEMP(I),TIME(I),FLO(I),WL(I)
46      101 FORMAT(I6,4F15.1)
47      1000 CONTINUE
48      WRITE(6,15)
49      DO 2000 I=1,9
50      MUMIX=1.2812/10.0**5*(TEMP(I)+273.0)**(0.5)/OMEGAV(TEMP(I),113.0)
51      RHOMIX=3.8997/10.0/(TEMP(I)+273.0)
52      NUMIX=MUMIX/RHOMIX
53      D12=2.3989/10.0**5*(TEMP(I)+273.0)**(1.5)/OMEGAD(TEMP(I),182.45)
54      NSC=NUMIX/D12
55      S=FLO(I)/(0.25*3.14159*2.9*2.9)/60.
56      NRE=S/NUMIX*1.4697
57      NSH=2.0+0.6*NRE**0.5*NSC**0.333
58      KM=NSH*D12/1.4697*RHCMIX/32.0
59      PT(I)=1.0
60      X(I)=1.0
61      KEQ=SQRT(10.0**(-24700/(TEMP(I)+273.))+6.2))
62      A=1.0/((2.*3.14159*100.**8.317*10.**7*(TEMP(I)+273.))**0.5)
63      AA=A*100.*KEQ*(PT(I)*X(I)*1.0133*10.**6)**(0.75)*(1.0133*10.**6)**
      1 (.25)
64      BB=A*(PT(I)*1.0133*10.**6)/KM

```

```

65      RC(I)=AA/(1.0+88)
66      RE(I)=WL(I)/1000./TIME(I)/3600./(3.14159*1.2*1.2)*2.*100./152.
67      WRITE(6,20) I,NSC,NRE,NSH,BB,KM,RE(I),RC(I)
68      RE(I)=ALCG10(RE(I))
69      RC(I)=ALOG10(RC(I))
70      2000 CONTINUE
71      WRITE(6,210)
72      210 FORMAT(1H1,1X,'STEARNS EXP. DATA : 1/2CR2O3(S) + 3/4C2(G) = CR03(G
      1)'//', NC.      TEMP(C)      PTOTAL(TORR)      PO2(TORR)      RATE(G
      2M OF CR/CM**2-HOUR)'//')
73      MCR=52.0
74      MCRO3=100.0
75      FACTO=MCRO3/MCR
76      DO 220 I=1,11
77      READ(5,230) TE(I),PO2(I),RR(I)
78      230 FORMAT(F10.0,F10.3,F10.2)
79      IF(I.GT.5) GO TO 240
80      PO2(I)=10.0**PO2(I)
81      RR(I)=10.0**RR(I)
82      GO TO 250
83      240 RR(I)=RR(I)/10.0**5
84      250 PTOT=0.115
85      WRITE(6,260) I,TE(I),PTOT,PO2(I),RR(I)
86      260 FORMAT(14,F13.0,F12.3,F15.3,E20.3)
87      PO2(I)=PC2(I)/760.0
88      RR(I)=RR(I)/(60.0*60.0)*FACTO
89      220 CONTINUE
90      WRITE(6,270)
91      270 FORMAT(1H1,' NO.      OBS. RATE      PRED. RATE(GM OF CR03/CM**
      12-SEC)'//')
92      DO 280 I=1,11
93      A=1.0/SQRT(2.0*3.14159*100.0*8.317*10**7*(TE(I)+273.0))
94      KEQ=SQRT(10.0**(-24700.0/(TE(I)+273.0)+6.20))
95      RP(I)=A*100.0*KEQ*PO2(I)**(0.75)*1.0133*10**6
96      WRITE(6,290) I,RR(I),RP(I)
97      290 FORMAT(14,E17.3,E21.3/)
98      RR(I)=ALCG10(RR(I))

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99      RP(I)=ALGG10(RP(I))
100     280 CONTINUE
101     WRITE(6,310)
102     310 FORMAT(1H1,1X,'HAGEL EXP. DATA IN STATIC OXYGEN : 1/2CR2O3(S) + 3/
1402(G) = CR03(G)'//', NO.      TEMP(C)      PTOTAL(MM-HG)      PO2
2(MM-HG)      RATE(GM OF CR2O3/CM**2-SEC)'//')
103     DO 320 I=1,6
104     READ(5,330) TEMP(I),PTOTAL(I),PO2(I)
105     330 FORMAT(3F10.0)
106     RR1(I)=0.214*EXP(-48800.0/((1.987*(TEMP(I)+273.0)))
107     WRITE(6,340) I,TEMP(I),PTOTAL(I),PO2(I),RR1(I)
108     340 FORMAT(14,F14.0,F13.0,F17.0,E22.3)
109     PTOTAL(I)=PTOTAL(I)/760.0
110     PO2(I)=PO2(I)/760.0
111     RR1(I)=RR1(I)*2.0*100.0/152.0
112     320 CONTINUE
113     NN=6
114     321 WRITE(6,350)
115     350 FORMAT(1H1,1X,' NO.      NSC      NPR      NGR      NNU      RX./
1MASS TRANS.      OBS. RATE      PRED. RATE(GM OF CR03/CM**2-SEC
2)'//')
116     DO 360 I=1,NN
C
C      CALCULATE CONVECTIVE HEAT TRANSFER COEFFICIENT BY FIRST CALCULATE
C      THE GRASHHOF NUMBER AND PRANDTL NUMBER. BY FOLLOWING WIMBER'S PAPER
C      THE PROPERTIES OF OXYGEN WERE DETERMINED AT FILM TEMPERATURE EQUAL
C      THE AVERAGE OF SAMPLE TEMPERATURE AND AMBIENT FREE STREAM TEMP.
C
117     TF=0.5*(TEMP(I)+273.0+300.0)
118     BETA=((TEMP(I)+273.0)/298.0-1.0)/(TEMP(I)-25.0)
119     DENST=PO2(I)*32.0/(82.057*TF)
120     L=1.7145
121     IF(NN.EQ.7) L=2.0
122     G=980.0
123     VISCT=1.2812/10.0**5*SQRT(TF)/OMEGAV(TEMP(I),113.0)
124     GR=BETA*G*DENST**2*L**3*(TEMP(I)-25.0)/VISCT**2
125     CP=8.27+C.000258*TF-187700.0/TF**2

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126      CONDUCT=(CP+2.484)*(VISCT/32.0)
127      PR=VISCT*CP/CONDUCT/32.0
      C
      C   CALCULATE NUSSELT NUMBER FROM CORRELATION FOR NATUAL CONVECTION
      C   IN VERTICAL PLATE. WELTY,WICKS,WILSON P.338
      C
128      NU=0.678*(PR/(0.952+PR)*GR*PR)**(0.25)
129      H=NU*CONDUCT/L
      C
      C   CALCULATE DIFFUSIVITY AND CALCULATE MASS TRANSFER COEFFICIENT BY
      C   CHILTON-COLBURN ANALOG. WELTY,WICKS,WILSON P.550
      C
130      D=2.3989*(TEMP(I)+273.0)**(1.5)/10.0**5/OMEGAD(TEMP(I),182.45)
      1/PTOTAL(I)
131      PRDSC=CP*DENST*D/CONDUCT/32.0
132      SC=PR/PRDSC
133      KGI=H*PRDSC**((2.0/3.0)*32.0/(DENST*CP))
134      KM=KGI*PTOTAL(I)/((82.057*(TEMP(I)+273.0))
135      KEQ=SQRT(10.0**((-24700.0/(TEMP(I)+273.0)+6.20))
136      A=1.0/SQRT(2.0*3.14159*100.0*8.317*10.0**7*(TEMP(I)+273.0))
137      AA=A*100.0*KEQ*PD2(I)**(0.75)*1.0133*10**6
138      C=A*PTOTAL(I)*1.0133*10**6/KM
139      IF(NN.EQ.7) GO TO 365
140      RP1(I)=AA/(1.0+C)
141      WRITE(6,370) I,SC,PR,GR,NU,C,RR1(I),RP1(I)
142      370 FORMAT(I6,F8.2,F9.2,F9.2,F9.2,E19.3,E20.3,E29.3/)
143      RR1(I)=ALOG10(RR1(I))
144      RP1(I)=ALOG10(RP1(I))
145      GO TO 360
146      365 RP2(I)=AA/(1.0+C)
147      WRITE(6,370) I,SC,PR,GR,NU,C,RR2(I),RP2(I)
148      RR2(I)=ALOG10(RR2(I))
149      RP2(I)=ALOG10(RP2(I))
150      360 CONTINUE
151      IF(NN.EQ.7) GO TO 361
152      WRITE(6,410)
153      410 FORMAT(1H1,1X,'KOHL EXP. DATA IN SLOWLY FLOWING OXYGEN : 1/2CR2O3(

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15) + 3/402(G) *CR03(G)*/// NO.      TEMP(K)      PTOTAL(MM-HG)
2  PO2(MM-HG)      RATE(MICRO GM/CM**2-HR)*///

154      NN=7
155      DO 420 I=1,NN
156      READ(5,430) TEMP(I)
157      430 FORMAT(F5.0)
158      RR2(I)=3.98*10.0**8*EXP(-48400/(1.987*TEMP(I)))
159      PTOTAL(I)=750.0
160      PO2(I)=750.0
161      WRITE(6,340) I,TEMP(I),PTOTAL(I),PO2(I),RR2(I)
162      PTOTAL(I)=PTOTAL(I)/760.0
163      PO2(I)=PO2(I)/760.0
164      RR2(I)=RR2(I)/3600.0/10.0**6*FACTO
165      TEMP(I)=TEMP(I)-273.0
166      420 CONTINUE
167      GO TO 321
168      361 CONTINUE
169      CALL GRAPH(31,K1,K1C,1,107,-7.,-7.,5,-9.6,5,-9.6,'OBS. RATE;',
1'PRED. RATE;', 'CR203 OXIDATION;', 'GRAHAM DATA;')
170      CALL GRAPHS(9,RE,RC,2,107,'CAPLAN DATA;')
171      CALL GRAPHS(11,RR,RP,12,107,'STEARNS DATA;')
172      CALL GRAPHS(6,RR1,RP1,10,107,'HAGEL DATA;')
173      CALL GRAPHS(7,RR2,RP2,5,107,'KGHL DATA;')
174      STOP
175      END

176      FUNCTION GMEGAV(T,EPCK)
177      TS=(T+273.0)/EPCK
178      A=1.16145
179      B=0.14874
180      C=0.52487
181      D=0.77320
182      E=2.16178
183      F=2.43787
184      R=-6.435/10.0**4
185      S=18.0323
186      W=-0.76830

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187      P=7.27371
188      OMEGAV=(A/TS**B)+C/EXP(D*TS)+E/EXP(F*TS)+R*TS**B*SIN(S*TS**W-P)
189      RETURN
190      END

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191      FUNCTION OMEGAD(T,EPOK)
192      TS=(T+273.0)/EPOK
193      A=1.06036
194      B=0.15610
195      C=0.19300
196      D=0.47635
197      E=1.03587
198      F=1.52996
199      G=1.76474
200      H=3.89411
201      OMEGAD=(A/TS**B)+C/EXP(D*TS)+E/EXP(F*TS)+G/EXP(H*TS)
202      RETURN
203      END

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