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Coal Gasification: A Materials Review

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COAL GASIFICATION: A MATERIALS REVIEW

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ABSTRACT

The development of sulfidation resistant alloys for coal conversion will require closely coupled pilot plant operations and laboratory investigation to meet current US energy goals in a timely fashion. A review of existing information regarding sulfidation damage in other commercial systems and experimental studies suggest that aluminum, molybdenum, and silicon additions as well as trace additions of rare earth elements can provide increased sulfidation resistance and component lifetimes during harsh coal gasification exposures. Advanced studies are required to assure that addition of protection elements will not induce significant fabrication (forming, welding, etc.) problems.

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PROBLEM DEFINITION

The desire of the United States to become energy independent presents a formidable challenge to the engineering community. In addition to the challenge of developing new processes and solving the associated design, fabrication, construction, and materials problems, the uncertain political atmosphere places severe time constraints on meeting the energy development goals. The US can no longer afford the luxury of using 25 to 30 years to develop new energy sources. For instance, another Arab oil embargo or an embargo by any country controlling critical materials for energy development could result in increased pressure to accelerate energy development and/or a drastic reduction in energy consumption with a concommitant lowering of our standard of living.

The use of coal appears to be the best solution to meet quickly our near-term needs (5-10 yrs) because of its relative domestic abundance and because there already exists a technological base in coal conversion in the U.S. However, coal technology as it exists today is incapable of supplying the required amounts and forms of energy required. The results is a necessary acceleration of coal conversion development in all areas of coal processing from mining to coal gasification and liquefaction. The development of coal gasification has proceeded to date as a process development study with the major goal of defining the process conditions required to produce both low BTU and high BTU synthetic gas. Nearly all the funding for this development has been allocated for process studies from bench scale to pilot-sized plants. Approximately 1% of the fossil energy budget has been appropriate to evaluate materials

compatibility in these heretofore unexplored environments of high pressure, temperature and corrosive gases. A notable part of this program is the study[1] at Illinois Institute of Technology Research Institute (IITRI) where candidate alloys are being exposed to a typical coal gasification environment. The initial results of this study indicate that few alloys exhibit sufficient hot gas corrosion resistance to survive extended life in a commercial gasification facility. Further, the most promising alloys are expensive and in short supply. This situation could be further aggravated because these alloys contain high levels of nickel and chromium for which the US must depend on foreign countries to supply.

The state-of-the-art for hot gas corrosion produced during long-term exposures in coal gasifiers will be reviewed in this paper. We will focus primarily on the effect of sulfur since the largest portion of easily accessible coal is sulfur laden and experience has shown sulfidation to be a primary cause of material degradation. Unfortunately, the kinetics of combined oxidation and sulfidation of highly alloyed materials in industrial combustion atmospheres has received little attention. Studies in coal gasification atmospheres, with the exception of the IITRI program, are largely nonexistent. As a result, we have considered related investigations to help identify possible ways of improving available alloys or developing new alloys for survival in coal gasification environments.

Several cogent reviews[2,3,4,5,6] have been written on hot gas corrosion and sulfidation of alloys. Attempts to describe hot gas corrosion processes with a unified corrosion mechanism have been unsuccessful except when pure metals are exposed to a single component gas. A major reason for this lack of success is the complex nature of the problem. This complexity is particularly evident in sulfidation studies where: (1) many stable sulfides can form in an exposed

alloy system, (2) the sulfides may have low melting temperatures, (3) they may form metal sulfide eutectics, and (4) sulfides are more voluminous than oxides leading to pore formation and cracking. In addition, coal gasification utilizes complex, multicomponent alloys to contain multicomponent gases at high temperatures and pressures. As a result of not having a satisfactory theoretical description of hot corrosion processes and complex operating conditions, it is difficult to predict a priori optimum alloy composition. As a guide for future activities, this review will summarize past studies and discuss factors which should be usefully applied to alloy development.

STATE-OF-THE-ART SUMMARY

How can one expect alloys to perform when exposed to hot gas corrosion conditions found in coal gasification atmospheres? Preliminary results of the IITRI[1] corrosion study suggest few uncoated (aluminized or chromized) commercial alloys provide low corrosion rates over extended life-times. Precoated alloys, while performing well in laboratory tests, suffer from important deficiencies: (1) coatings interfere with welding operations, (2) field welds cannot be easily recoated, and (3) spallation or erosion of a coating would eventually expose the underlying alloy and leave it unprotected. A more desirable condition would be one where the alloy itself produces a protective surface layer in the environment which can be reformed in the event of erosion or crack initiation.

While performance data concerning the hot corrosion alloys being used for other commercial applications is informative, important differences in operating environments exist. Coal gasification environments have higher

sulfur activities and lower oxygen activities than those encountered in gas turbines. Further, the temperature regimes are generally higher than those experienced in boilers, desulfurizers and other fuel burning equipment. Also, the following literature survey will show that: (1) no general models for hot gas corrosion have been developed to predict the behavior of available alloys in coal conversion environments or guide development of new alloys, and (2) much of the experimental data reported is in conflict.

Despite the apparent confusion in the existing literature, several guidelines for empirical alloy development seem apparent. First, nearly all studies involving the effect of chromium level on corrosion in H_2S, SO_2, S vapor and Na_2SO_2 suggest that Cr contents between 20 and 30 percent are required. The IITRI results suggest a 25 percent minimum. Chromium must be present in sufficient concentrations to form a continuous Cr_2O_3 scale and not fine Cr_2O_3 precipitates due to internal oxidation. High levels of chromium are beneficial for corrosion resistance and rehealing of cracked scales. However, penalties in fabricability and weldability usually result. Secondly, in gaseous atmospheres and with slagging absent, Al should improve sulfidation resistance, especially if the alloys are preoxidized after construction. Al_2O_3 and Cr_2O_3 provide protective layers for reducing potential oxidation contributions to corrosion in hot coal gasification environments in addition to being a barrier for sulfur diffusion. As will be discussed in the following literature review, Mo additions and possible Si additions, have been observed to act as layer or scale dopants to improve sulfidation resistance either by reducing the outward diffusion of metal ions or by retarding the growth kinetics of the oxide scale initially formed. However, the use of Mo should be carefully checked for the possibility of MoO_3 formation and subsequent volatilization at temperatures greater than 800°C. The addition of trace amounts of rare earth elements, particularly La, Ce, and Y has led to improved sulfidation resistance in gas turbine environments. A review

of the literature on the effect of rare earth additions suggest that these elements tend to reside in grain boundaries where they can possibly "block" diffusion of sulfur and reduce intergranular penetration, thereby eliminating a short circuit path for sulfur to reach deep into an alloy. However, the residual effects of rare earth on fabrication and welding will need to be clearly established to permit their use in commercial systems.

The lack of information in the literature concerning hot gas corrosion of weldments is particularly disappointing. In highly alloyed steels or nickel-base alloys, the "cast-type" microstructure of welds will corrode differently than parent materials. Grain boundary sensitization, coring, and other alloy segregation events which occur within welds and heat affected zones can affect sulfidation resistance. It would be presumptuous to predict hot gas corrosion performance of weldments from unwelded data. Preliminary weld results from the IITRI study indicate differences in sulfidation behavior of welds compared to unwelded samples, particularly along the heat affected zone. Hot corrosion in weldments clearly needs greater attention to assure reliable system performance.

The following discussion will not consider the additional complicating effects of: (1) carburization and nitridation on sulfidation resistance, (2) highly reducing environments, (3) thermal and mechanical cycling, and (4) surface condition. Although the scope of this paper does not include discussion of these variables, it should be pointed out that these aspects might become important factors in alloy performance in a commercial gasifier. The discussion will point out, however, that alloy development for coal conversion applications is dependent on a broad range of variables. Given sufficiently long times, it might be possible to study each effect and develop theoretical performance models. However, in the short term, we have to rely on the corrosion results of specimens exposed to actual pilot plant conditions

and on empirical methods for alloy selection. Laboratory studies should proceed concurrently with sufficient flexibility to consider any important effects that surface from analysis of specimens exposed in pilot plants. On the other hand, pilot plant operations should be flexible enough to handle specimens of new alloys which exhibit promising characteristics in laboratory tests. Without cooperative efforts by laboratory and pilot plant personnel, it is doubtful that long life alloys will be developed in time to meet the construction schedules of commercial coal gasification plants.

LITERATURE SURVEY AND DISCUSSION

Fundamental Studies

Fundamental studies of parabolic sulfidation and oxidation scaling of metals has been conducted by Wagner[7] and subsequently updated by others[4,5,8]. A synopsis of the cogent parts of the reaction models and the fundamental processes is beyond the scope of this report, and the reader is advised to consult these references for details. In general, most theories describe scaling mechanisms in terms of one of several rate-controlling steps which include: (1) S diffusion through the gas phase boundary layer, (2) anion diffusion of O^- or S^- inward through the scale, or (3) metal cation diffusion outward through the scale. The driving forces for sulfidation are the free energy of formation for the sulfide (or oxide) layer formed and the chemical potential across the scale. In environments where partial pressures of both sulfur and oxygen exist, the growth characteristics of the scale reflect the competition between their sulfidation and oxidation potentials. Generally, the free energy change for oxide formation exceeds that for sulfide formation and oxides form initially[4,8,11]. However, sulfur penetration through an oxide

layer via bulk diffusion or along grain boundaries, cracks, pores, and other defects within the oxide can yield the necessary thermodynamic conditions (i.e., sufficient sulfur activity) for sulfide formation below the oxide layer. A good discussion of defect structures in sulfides has been written by Stafford[2]. Gaseous corrosion at elevated temperatures via oxidation or sulfidation is related to the defect structure[2,3,5] and the number of defects present in the oxide or sulfide scales. A low defect concentration appears necessary for effective protection.

Analysis of sulfidation of pure metals and alloys using classical thermodynamics is largely nonexistent except in single component gases. This lack is due to the complexity of the problem and the fact that observed scale formations do not agree with those predicted for equilibrium conditions[3]. Petit, Goebel, and Goward[9] have treated the problem of corrosion in the presence of two oxidants. The first, oxygen, causes the formation of an oxide scale as would be expected from classical thermodynamics. The second oxidant, SO_2, may form a second oxide at the scale/metal interface where equilibrium oxygen partial pressure approaches that coexisting between the metal and the second oxide. Pettit et al.[9] point out that the second compound can form within the scale as well. Similar conclusions were reached by Ross[12].

Mar[10] extended the Pettit analysis to the case of two oxidants and two solutes, in an effort to provide insight into selecting solutes which will form discrete oxide/sulfide layers. The gaseous equilibrium conditions were used only to establish chemical activites of oxygen and sulfur at the surface, and internal scale formation conditions were referred to activity gradients extending into the metal. By so doing, the kinetic aspects of oxidation/sulfidation were integrated into classical thermodynamic calculations. Based upon evidence in

the literature, Mar assumed Cr and Al to be the solutes required for protective oxide formation. Secondary solutes which promoted the formation of sulfide layers were predicted to be the alkaline earths, rare earths, and elements from groups III B, IV B, and V B. Rahmel and Gonzalez[11] have also described thermodynamically the formation of oxide and sulfide phases relative to SO_2 and O_2 partial pressures. They conclude that when an oxide scale initially forms, the oxygen partial pressure decreases in the scale with distance from the gas/scale interface. As a result, the sulfur partial pressure can increase at the scale/metal interface where sulfides can form. Thus, the formation of sulfides, which are not predicted by thermodynamic analysis, can occur. It is clear that both kinetics and thermodynamics need to be considered simultaneously to accurately describe corrosion in hot gases.

The list of variables influencing sulfidation rates includes temperature, pressure, exposure time, gas composition, surface condition, metal composition, scale morphology, plasticity of scales, slag formation and others. The list itself demonstrates the complexity of the problem without considering the complexity within each individual variable. It is extremely difficult to generalize the effect of specific variables on sulfidation rates because of mutual interactions between them.

Environmental Variables

The influence of temperature on sulfidation rates is demonstrated in Figures 1 and 2 for Ni-Cr alloys[13]. In a given atmosphere, increased temperatures usually result in increased corrosion rates in most alloy systems[14,15,16] providing that the rate controlling step remains the same and other influences such as slagging and liquefaction do not intervene.

While sulfidation studies are usually conducted at ambient pressures, except in turbine burner hot corrosion tests, increasing the total system

pressure increases sulfidation rates. Generally this effect is monitored by increasing the partial pressure of the sulfur bearing species as shown in Figure 3[17]. Preliminary results of the IITRI study[1] suggest that increasing the total pressure with constant gas composition strongly increased sulfidation rates. Increased corrosion rates are likely due to increased partial pressure of sulfur[17] and/or thermodynamic equilibrium changes resulting from high pressures[18]. Nateson[18] indicates that total pressure increases can shift the phase boundaries in the Ellingham equilibrium diagrams. He argues that the environmental conditions existing in most coal gasification pilot plants are typically near a phase boundary on the Ellingham diagrams, and therefore, the influence of pressure can move the reactions to phase regions where different scales are thermodynamically preferred. Little work has been performed on the effect of pressure on the thermodynamic equilibrium of hot gas mixtures.

Experimental studies of sulfidation are usually conducted with the sulfur species appearing as H_2S, S vapor or SO_2. In industrial atmospheres, the sulfidant is usually H_2S (coal gasification), SO_2, (furnaces, boilers), or a sulfate such as Na_2SO_4 (formed by the combustion of ingested salts and sulfur containing fuels in engines and boilers). Corrosion due to pure S vapor is generally associated with laboratory rather than industrial environments. Neglecting sulfate forming processes, the severity of corrosion of alloys follows this ranking from most to least severe[19,20]: H_2S, S vapor, SO_2. Seybolt[21] observed that corrosion of nickel-base super-alloys was generally greater in H_2S/H_2 atmospheres than in liquid Na_2SO_4. This fact has clear experimental benefits because of the ease with which one can conduct studies in H_2S or S vapor atmospheres compared to complex industrial combustion atmospheres. The drawback, of course, is that testing in H_2S/H_2 mixtures

or S vapor doesn't result in simultaneous exposure to both oxidizing and sulfidizing conditions.

Alloy Composition

A. Iron Base Alloys

Strafford and Manifold[19] studied the corrosion behavior in S vapor of Fe and binary Fe alloys containing 5 wt.% Ni, Co, Cr, or Al. The addition of 5 wt.% of any of the four elements resulted in decreased corrosion relative to pure Fe and the development of duplex scales compared with the formation of a single FeS scale on pure Fe. These results suggest that scale growth occurs primarily by Fe cation diffusion through the scale in the case of pure Fe. Cr and particularly Al, proved to be the best alloy additions to reduce corrosion in Fe as shown in Figure 4. Generally the scales formed on the alloyed Fe were compact and adherent. Duplex scales were observed on the Fe-Al and Fe-Cr alloys with the inner scale containing a significant amount of alloying element. In both cases a striated inner scale was observed which consisted of alternate Cr (or Al) rich bands and Fe rich bands. The Al or Cr alloying elements were not observed in the outer FeS scale. The Fe-Ni and Fe-Co alloys showed a duplex FeS scale containing only minor levels of Ni can Co in solution. The large reduction in reaction rates in The Fe-Cr and Fe-Al alloys was associated with the formation of compact diffusion barriers of FeS containing either Cr_2S_3 or Al_2S_3. Strafford and Manifold[19], conclude that the improved resistance when Cr or Al are alloyed with Fe results from preferential sulfidation of these elements. The alternate banding of the inner layer is rationalized by the tendency of Cr or Al to sulfidize preferentially as the activity of the Al or Cr cycles during sulfidation with the opposite occurred in the activity of the Fe. This situation is similar to that described earlier for duplex layer formation in an environment containing two oxidants. Long-term

scale growth was observed by Strafford and Manifold[19] to be controlled by Fe cation diffusion and obeyed parabolic reation kinetics.

Hauffe[5] suggests that sulfur-sensitive alloys be plated with aluminum because Al is relatively stable in the presence of sulfur. The IITRI work[1] supports this conclusion. Flatley and Birks[22] observed high rates of attack of SO_2 on Fe due to the formation of lamellar scale structure of alternate sulfide and iron oxide layers. They observed that the time to form a protective oxide layer decreases as the atmosphere becomes more oxidizing, indicating that preoxidation would at least delay the onset of sulfidation. However, this initially protective layer is inadequate for long-term exposures due to the occurrence of oxide-sulfide eruptions once sulfur is able to penetrate the oxide. Salisbury and Birks[23] showed that Cr additions up 15 wt.% improved sulfidation resistance of Fe in SO_2 atmospheres. Companion studies conducted in pure O_2 showed much lower scaling rates. The reduced oxidation resistance in SO_2 is attributed to the formation of chromium sulfides at the metal/oxide interface which denudes the adjacent matrix of Cr. Cr contents greater than 10% were required to avoid extensive sulfide formation at the interface during 2 hour exposures. High Cr steels (>20%) have also been shown to be resistant to SO_2 atmospheres[4,24]. Young and Smeltzer[16] studied the effect of cobalt additions in iron exposed to H_2S/H_2 atmospheres and observed increasing reaction rates with Co additions. Their results verified that sulfidation was controlled by lattice diffusion of iron through the sulfide layer and obeyed Wagners parabolic scaling theory.

Rahmel[25] studied the scaling of iron and steel in environments containing two oxidants, one of which was sulfur bearing. His study showed that simultaneous formation of oxides and sulfides can occur when the rate determining step is diffusion in the scale/gas phase boundary. In this case two oxidants increase

the scaling rate. However, when diffusion of Fe ions through the scale controls, the most thermodynamically stable phase, either oxide of sulfide, forms preferentially and the presence of a second oxidant does not affect the scaling rate. This would imply that preoxidation of steels would reduce sulfide formation in sulfur bearing gases. Practically, however, thick, compact, crack-free oxide layers would be required for exposure at temperatures above 900°C, a situation which is difficult to guarantee.

B. Nickel-Base Alloys

Nickel-base super-alloys[21,26-31] have received more attention in recent studies because of attractive mechanical properties and oxidation resistance at elevated temperatures. Pure nickel corrodes very rapidly in H_2S at 900°C obeying linear rate kinetics as demonstrated by Hancock[26]. The scale formed was primarily Ni_3S_2. In recent paper, Bastow and Wood[15] observed that four corrosion layers formed during exposure of pure nickel to S vapor at 400-475°C. Scale growth obeyed a parabolic law for the three outer layers and they interpret the formation of a multilayer scale in terms of diffusion controlled processes. These results are in disagreement with those of Czerski et al.[27] who observed a predominately NiS scale. Thus, controversy exists even within studies of pure metals in sulfur-bearing environments.

Aluminum[5] and chromium[17,29-31] effectively increase sulfidation resistance in nickel especially in concentrations greater than 15%. A comprehensive investigation by Mrowec et al.[13] considered sulfidation (S vapor) of Ni containing from .11% to 82% Cr. They observed that alloys containing less than 2% Cr corroded faster than pure nickel while those having greater than 20% Cr corroded slower than pure chromium. A summary of their results is presented in Figures 2 and 5. As the temperature approaches 1000°C (Figure 5), the optimum composition for minimum sulfidation appears to lie between 50-60% Cr. In

addition, recent studies indicate that 50Cr-50Ni exposed to a typical coal gasification atmosphere containing 1.0% H_2S exhibits more corrosion resistance than 15 other stainless steels and nickel-base high temperature alloys[1]. Mrowec[13] et al. suggest that alloy composition is the most important controlling factor in determining sulfidation mechanisms. They site four regions of alloy composition (Figure 6) which have different controlling mechanisms that are not markedly influenced by temperature. In alloys containing less than 2% Cr (region I) the scale is single-phase with Cr in solution and the rate-determining step is the outward diffusion of nickel ions. In alloys having greater than 40% Cr (region IV) the controlling step is outward diffusion of Cr ions. With intermediate concentrations of Cr (regions II and III) simultaneous diffusion of metals cations and sulfur anions predominates. In alloy compositions typical of commercial alloys, region II, a heterogeneous scale consisting of both nickel and chromium sulfides is formed with the outer layer being $Ni_{1-x}S$. In these alloys increased corrosion resistance is due primarily to the formation of a Cr_2S_3 layer.

To improve sulfidation behavior of Ni-Cr alloys, Young et al. suggest the addition of molybdenum[17]. Small molybdenum additions have been reported by Strafford and Hampton[30] to increase the sulfidation resistance of chromium. Young et al.[31] observed that sulfidation rates for a Ni-20% Mo alloy were two orders of magnitude lower than those in Ni-20%Cr alloy under the same exposure conditions (low sulfur partial pressures). However, at partial pressures, $P_{S_2} > 1 \times 10^{-10}$ atm., the reverse is true because of liquid phase ($Ni_{3+x}S_2$) formation. It appears that Mo in pure nickel is detrimental to sulfidation protection in coal gasification atmospheres where P_{S_2} is typically greater than 10^{-10} atm. Young et al.[17] studied the effect of molybdenum additions on the sulfidation properties of Ni-20% Cr and Ni-30% Cr. Their

studies indicate Mo additions (2-10%) improve the scaling characteristics of Ni-Cr alloys at 700°C in H_2S/H_2 atmospheres. They conclude that the addition of 10% Mo results in a beneficial effect in four specific ways: 1) with regard to internal sulfidation, Mo ($\geq$ 5%) reduces the rate at which sulfur diffuses into the alloy, 2) Mo ($\geq$ 5%) additions reduce the range of liquid sulfide formation (10% Mo suppressed liquid formation completely), 3) MoS_2 particles retard the outward diffusion of metal ions, and 4) Mo dissolves in Cr_2S_3 to reduce the outward metal diffusion through Cr_3S_3. If one considers the additional benefit of an oxide layer, which would be expected to form in coal gasification atmospheres, a Ni-30 Cr-10 Mo, should be an attractive candidate for coal conversion processes. The use of Mo should be checked carefully since molybdenum oxides, if they form, can be quite volatile above 800°C.

C. Stainless Steels

Much work has been performed on the reaction of stainless steels with hydrogen sulfide because of the extensive use of these steels for application such as catalytic reformers and desulfurizers. However, the majority of this work has been done at temperatures below 800°C. An early study by Nauman[32] showed high corrosion rates in 100% H_2S and also that increasing the Cr content improved the sulfidation resistance. Chromium levels of 20-30% appeared most desirable; however, at temperatures greater than 800°C the 300 and 400 series stainless steels were only resistant to sulfur in typical desulfurizer operating conditions when the H_2S level was very low[33]. Manganese-modified stainless steels have not been observed to exhibit better sulfidation properties than austenitic steels below 480°C and have inferior resistance at high temperatures[33]. High concentrations of nickel (>20%) appear to be undesirable in stainless steels. Nickel additions are acceptable in instances where the Ni concentration

is less than that of chromium[20] and where sulfidation is controlled by cation diffusion through the Cr_2S_3 scale. Nickel additions to various steels have been observed by Gruber[34] to decrease resistance to sulfidation in H_2S and SO_2 at temperatures to 1000°C. Thus it appears that nickel additions without accompanying chromium or manganese additions in stainless steels are undesirable.

In sulfur dioxide with very low moisture contents, stainless steels containing greater than 18% Cr (e.g. 304) perform well below 600°C. Again, higher Cr levels progressivly increase sulfidation resistance. Sulfidation by SO_2 in the presence of excess oxygen can result in accelerated scaling rates[4]. This acceleration could be due to mechanical cracking of the scale after a critical oxide thickness has been reached thereby permitting direct access to the underlying metal or due to chemical reduction of the chromium oxide layer after chromium denution in the metal surface occurs. Exposure of austenitic stainless steels to sulfur vapor or hydrogen sulfide is generally more severe than SO_2 exposure. As indicated in Table I, austentic stainless steels exhibit relatively high corrosion rates in S vapor. Note also that increasing the chromium concentration increases sulfidation resistance, as described earlier for H_2S and SO_2 exposures, with >20% Cr required to obtain corrosion rates less than 25 mils per year.

As pointed out by Morris[20], detailed laboratory studys of corrosion rates in typical combustion atmospheres is extemely difficult because of fluctuations in temperature and gas composition that occur within a single process unit. Thus field tests are necessary to assure compatibility with the corrosive environment. However, Morris does point out that successive increments in chromium content continually increases sulfidation resistance to typical combustion atmospheres (see Figure 7). Jackson, et al.[35] conducted an interesting study of sulfidation resistance of cast Fe-Cr-Ni alloys in sulfur

bearing flue-gas (both oxidizing and reducing) at temperatures to 2000°F. They also observed optimum sulfidation resistance in alloys containing at least 25% Cr and nickel contents between 10 and 20%. Increasing Ni levels beyond 15% produced severe corrosion in reducing atmospheres containing high levels of sulfur (>1 grain/cu.ft.). Further, they observed less attack in oxidizing flue gases than in reducing flue gases. Jackson[35] also studied the effect of cyclic variations in temperature on scaling in oxidizing flue gases. Samples were exposed for 100 hours at 980°C with a cool down to 150°C every 12 hours. This temperature cycling, in general, resulted in only minor increases in corrosion.

The effect of subjecting an alloy to alternating oxidizing and reducing flue-gas atmospheres was also studied by Jackson[35]. It is interesting that Jackson observed less attack in cyclic environments at 980°C than in either oxidizing or reducing flue-gas atmospheres. Finally, Jackson notes that additions of Si (1.5-2.5%) and Al (1-4.5%) produced strong increases in sulfidation resistance.

IITRI Materials Studies[1]

Several general conclusions regarding sulfidation in coal gasification atmospheres are apparent from the IITRI study:

1. A minimum of 25 percent chromium is required for good sulfidation resistance.
2. Aluminized surfaces on 310 stainless steel and Incoloy 800 reduced sulfidation rates under all conditions. Chromized surfaces also provide additional protection to sulfidation but they tend to form discontinuously and to spall.
3. The formation of slags on a specimen surface resulted in large increases in scaling rates.

While aluminized 310 and 50Ni-50Cr appear to be satisfactory for typical coal gasification atmospheres, in-situ pilot plant exposures are required to verify their use for extended periods. Further, detailed metallographic studies of the IITRI exposed samples are necessary to clearly discern the controlling scale formation mechanisms. Several incidents suggest that extrapolation of corrosion rates from 1000 hr. tests to the lifetime of a coal conversion facility is not straight forward[36]. It was observed in laboratory reactor exposures that aluminized 310 was susceptible to locally severe corrosion after a combined exposure of 4200 hours at 980°C, 1100 hours at 1000°C and 2400 hours at 815°C in coal gasification environments. Similarly 50Ni-50Cr was severely attacked in pilot plant exposure test. Detailed microstructural analysis of these samples would prove extremely helpful in alloy design. Further, pilot plant exposure of promising alloys must accompany laboratory studies to provide data which would aid the development of extrapolation techniques for predicting long-term behavior from laboratory results. Preliminary corrosion results of aluminized 310, aluminized Incoloy 800, 50Ci-50Ni and 309 (2000 hrs. at 980°C) suggest that the relative ranking of these materials is changed from their ranking after a 1000 hr. exposure[37].

Slag Formation

A complicating factor which has not been discussed thus far is the effect of slagging on sulfidation behavior. Slagging effects have been extensively studied during the development of gas turbine engine alloys. Accelerated attack results from the presence of liquid or solid sulfates (typically Na_2SO_4) or other slags (V_2O_5) formed during combustion of sulfur bearing fuel with air containing sea salts. The potential for slag formation leading to accelerated corrosion exists in coal gasification reactors although the exact nature and severity of the problem has not been established[38]. The varied operating

environments, alloys, and lifetime requirements of the different gasification processes require that each system be considered individually. Therefore, no general statements regarding the possibility of slag assisted hot corrosion can be made except that alloy development studies should include the effect of slag disposition on material performance.

Even with the massive efforts[40-44] to describe the effects of slagging on hot corrosion, no single mechanism has emerged to predict general alloy behavior. Two mechanisms, the alloy depletion mechanism[39] and acidic fluxing (oxide ion) mechanism[40,41] are currently receiving the greatest attention. The former is based on the role of sulfur with the hypothesis that the formation of chromium sulfide depletes the alloy matrix of chromium resulting in increased oxidation rates while the acidic fluxing theory argues that accelerated attack is due to the breakdown of the protective oxide layer by oxide ions in the deposited slag. Neither mechanism is adequate for explaining all the phenomena observed.

Kaufman[43] and most investigators report a minimum level of 15 percent Cr for adequate hot corrosion resistance with higher levels desirable. Morrow et al.[41] studied the effects of Al, Mo and Ti additions on hot corrosion of nickel-base alloys containing less than 15 percent Cr. Their findings suggest Mo to be beneficial at 870°C and more or less passive at 980°C. It is hypothesized that Mo enhances or assists the beneficial effect of Cr especially at Cr levels below 15%. Al additions were detrimental at both 1600°F and 1800°F. However, additions of Mo markly reduced the deleterious effects of Al. The effect of Ti additions appeared temperature dependent, being beneficial at 1600°F and detrimental at 980°C. Seybolt[39] made several interesting conclusions during his study of hot corrosion of ternary Ni-Cr-X alloys and commercial nickel-base superalloys. He studied the effects of 5 wt. percent additions of Al, Ti, Mo, and W in both

H_2S/H_2 and molten Na_2SO_4 environments. Interestingly Ni-20 Cr alloys with any of the additions showed a greater degree of attack compared to Ni-20 Cr, and that all four alloys were attacked less by the liquid sulfate than the H_2S/H_2 gas mixture at 1000°C. These results are in contradiction with those of Young et al.[17] who observed beneficial effects of Mo additions at lower temperatures, in gaseous environment. Seybolt[39] has shown that small additions of cerium (0.5 percent) are effective in preventing sulfide formation and overall corrosion of Udimit 500 (19Cr, 19Co, 4Mo, 3Ti, 2.9Al) at 950C for 1000 hours. Viswanathan's[45] studies of rare earth additions on hot corrosion of gas turbine alloys showed that trace additions of lanthanum (0.2 percent) and yttrium (0.2 percent) improved the sulfidation resistance of Udimit 700 (15Cr, 19Co, 5.2Mo, 3.5Ti, 4.3Al) at 815C.

Some controversy exists concerning the form of the rare earth additions. A subsequent study by Seybolt[39] on Ni-Cr alloys suggests that only rare earth addition in the form of oxides (CeO_2, La_2O_3, Gd_2O_3) are useful while in their metallic form, rare earth are of little benefit. Seybolt[39] observed that rare earth oxide additions suppressed formation of chromium sulfides in the scale whereas metallic rare earth addition did not. He postulates that the increased sulfidation resistance is due to gettering of the sulfur by CeO_2 and the subsequent formation of Ce_2O_2S. Since metallic rare earth additions can form intermetallic compounds of the form Ni_5X, where X is a rare earth, their usefulness is limited to situations where the Ni_5X is oxidized to X_2O_3 during the corrosion process. This oxidation step requires considerable energy. Similar results were reported for La and La_2O_3 additions.

Seybolt's results are in conflict with those of Viswanathan[44]. Viswanathan did not observed the formation of La_2O_3 in his microprobe examinations. Viswanathan postulates that rare earth additions may act to reduce the activity

on diffusivity of nickel in the alloy or act as barriers to inward diffusion of oxygen and sulfur at the grain boundaries. A similar effect of Si in Ni-20 Cr has been observed by others[44,19] where Si reduced nickel ion diffusion in Cr_2O_3. Thus the potential use of minor additions of rare earth elements to improve corrosion resistance in coal gasification environments appears to have some technical merit.

The use of metallic rare earth additions can lead to local liquation at temperatures above 1200°C, especially with Ce due to the eutectic formed between Ni and Ni_5X. La-Ni and Gd-Ni have higher eutectic temperatures than Ce-Ni and therefore liquation will not be a problem. Use of rare earth elements or rare earth oxides will present fabrication difficulties since incorporation of the metallic form in an alloy greatly reduces formability due to grain boundary embrittlement while powder metallurgy techniques are required to incorporate rare earth oxides in an alloy.

Other Potential Considerations

As mentioned earlier, several potentionally important considerations have received little attention in this paper. Potential carburization, decarburization, nitridation, surface condition, scale plasticity, spallation, sensitization of welds can limit performance in coal gasifiers. For instance, thermodynamic calculation show high carbon activities exist in typical coal gasification environments and suggest the possibility of carburization. Further Perkins[45], in his analysis of a failed recycle gas heater tube has shown that carburization played a significant role in the failure. This particular tube was exposed to a variety of complex gases at variety of temperatures such that it experienced different corrosion processes (oxidation, carburization, and sulfidation) during its history. While this particular exposure history is unlikely in any given

commercial process, the experience of this failure serves notice that synergistic effects are possible and that researchers need be aware of this possibility.

Similar arguments can be stated for the possibility of decarburization and its effect on sulfidation, especially in reducing atmospheres. Few studies exist where decarburization-sulfidation potentials exists simultaneously. Jackson et al.[35] has shown that decarburization resulted in his cast Fe-Ni-Cr alloys having less than 16 percent Cr in reducing flue gas environments accompanied by interdendritic corrosion penetration. Again, the synergistic effects are not clearly established. However, chromium levels in excess of 16 percent appear to be effective in reducing this type of attack.

This brief discussion admittedly suffers from a lack of detail regarding the many possible synergistic effects. Its purpose is to establish an awareness of other variables that may influence sulfidation and to encourage researchers to take a system approach to alloy design for coal gasification applications.

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TABLE I

CORROSION OF STAINLESS STEELS IN SULFUR VAPOR AT 1020°F

Material	% Cr	Corrosion Rate* (MPy)
314	23/26	16.9
310	24/26	18.9
309	22/24	22.3
304	18/20	27.0
302B	17/19	29.8
316	16/18	31.1
321	17/19	54.8

*Corrosion rates based on 1295 hr. tests, International Nickel Data.

TABLE II

GROUPING OF ALLOYS BY RATES OF CORROSION
IN THE HIGH TEMPERATURE, HIGH PRESSURE GASIFIER ENVIRONMENT

0.5 v/o H_2S			1.0 v/o H_2S		
Corrosion Rate, inches/year			Corrosion Rate, inches/year		
<.02	.02-.05	>.05	<.02	.02-.05	>.05
		1500°F, 1000 psi			
800	316	302	800	316	302
310	304	600	310	304	601
309		601	309		
446			446		
50/50			50/50		
314			314		
793			793		
800 (Al)			800 (Al)		
310 (Al)			310 (Al)		
		1800°F, 1000 psi			
800 (Al)	310	800	800 (Al)		800
446	310 (Al)	601	310 (Al)		600
50/50		600	50/50		601
		304			310
		309			309
		316			304
		793			302
					314
					316
					446
					793

Grouping based on 1000-hr. exposure extrapolated linearly to 1 year.

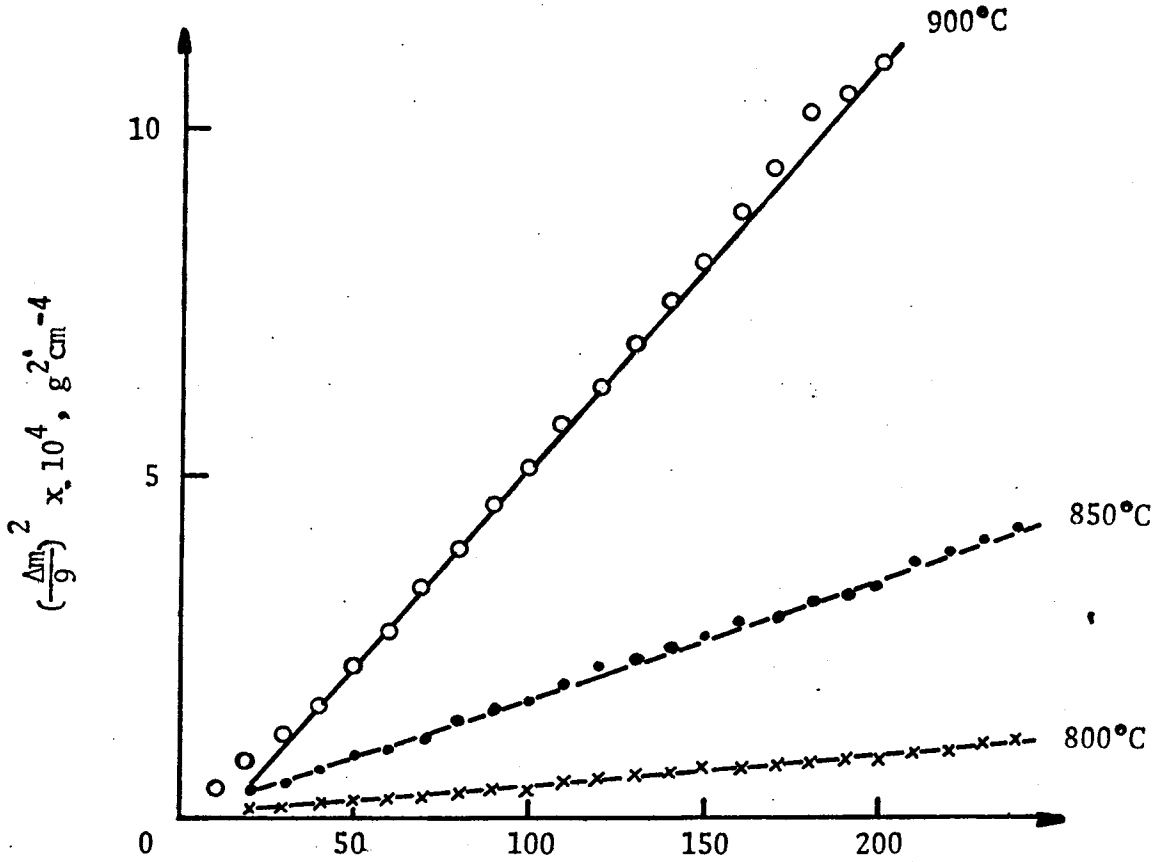

Figure 1. Parabolic plot of weight gain vs. time for alloys containing 63% Cr. (After Mrowec, et al., Ref. 13)

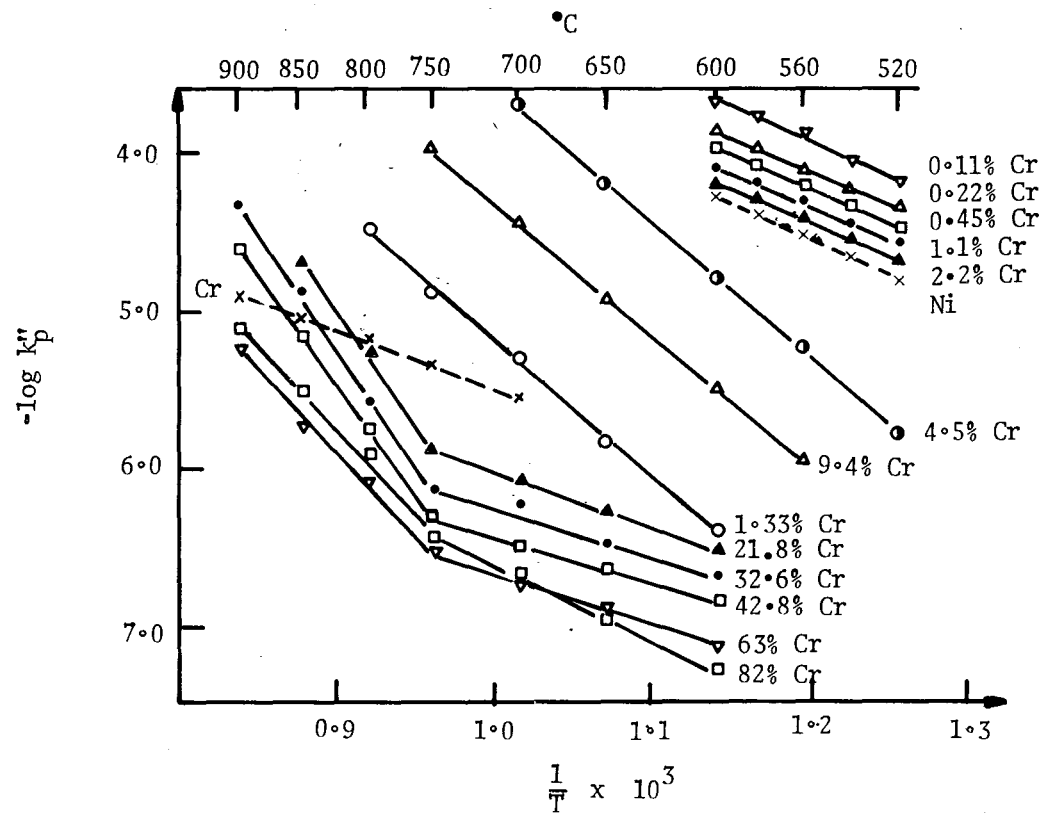

Figure 2. Dependence of sulphidation rate on temperature for Ni-Cr alloys. (After Mrowec et al., Ref. 13)

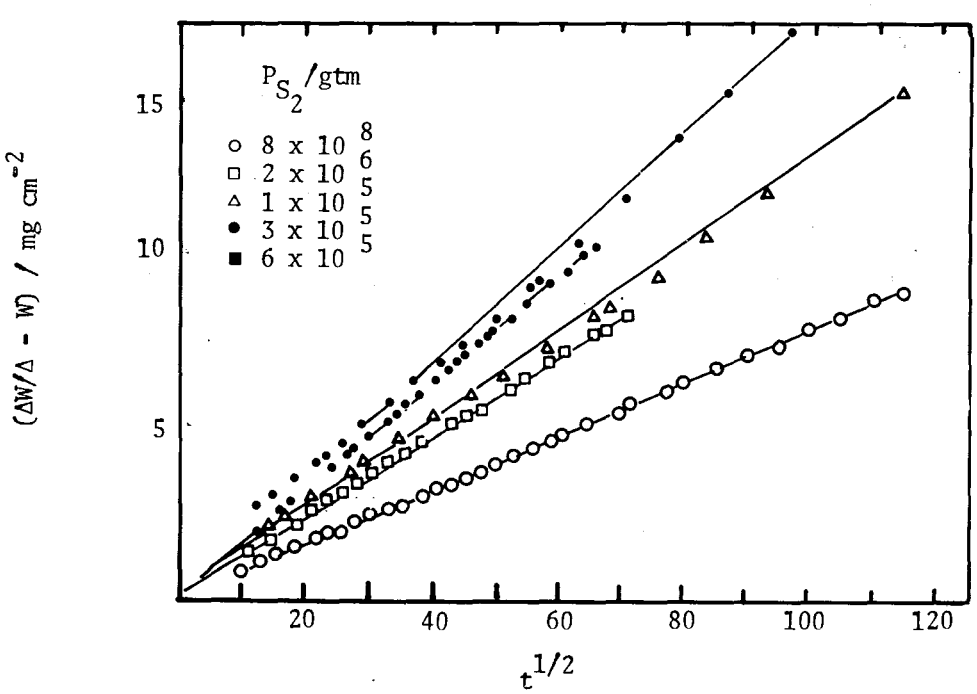

Figure 3. Parabolic plots of sulfidation kinetics of Ni-30 Cr 10 Mo in the external sulfidation region. (After Young, et al., Ref. 17)

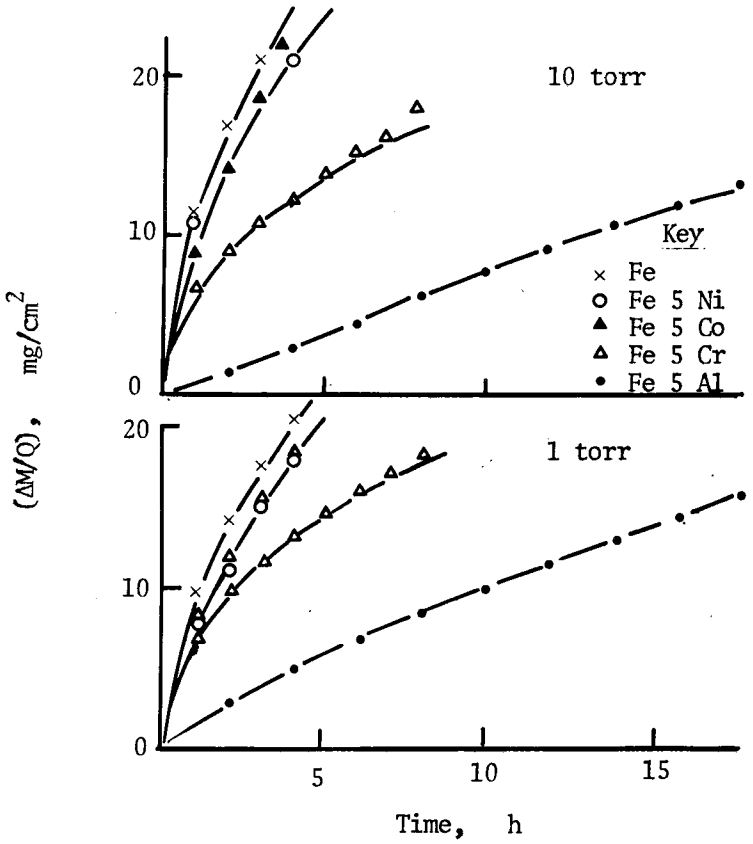

Figure 4. Weight-gain as a function of time during the sulphidation of Fe and the alloys Fe-5% Ni, Fe-5% Co, Fe-5% Cr and Fe-5% Al, at sulphur pressures of 1 and 10 torr. (After Strafford, Ref. 19)

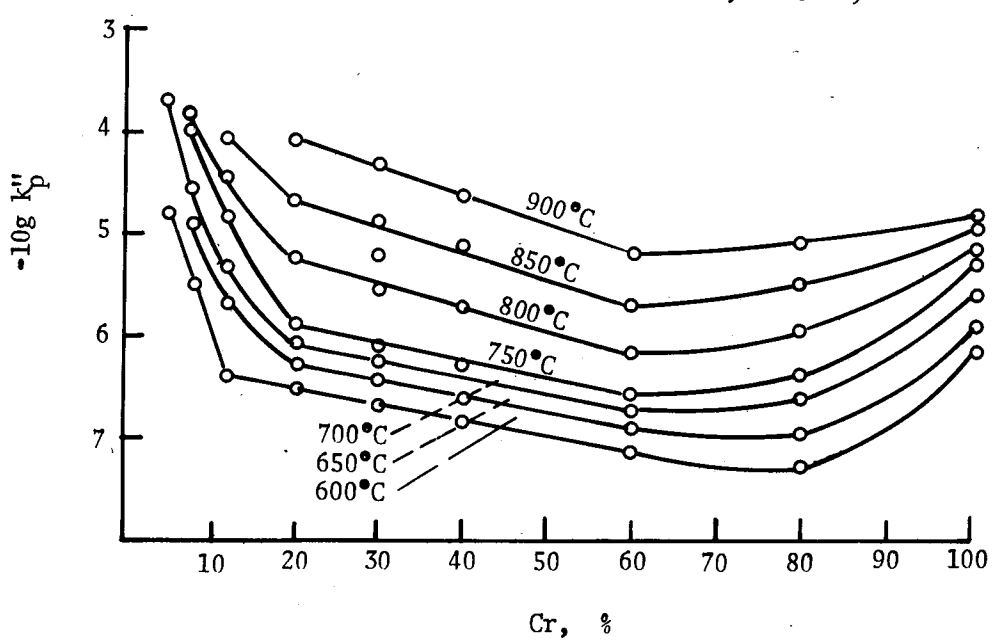

Figure 5. Dependence of sulphidation rate on chromium concentration for Ni-Cr alloys containing 4-5 82% Cr. (After Mrowec, et al., Ref. 13)

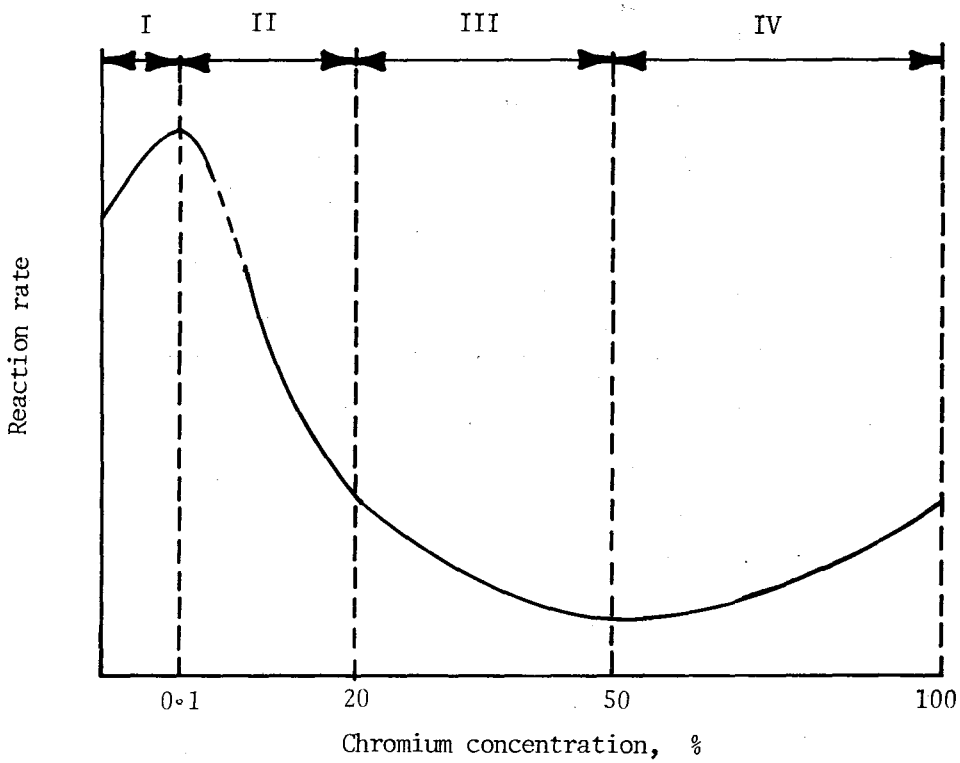

Figure 6. Schematic diagram of sulphidation rate as a function of chromium concentration in the alloy. (After Mrowec, et al., Ref. 13)

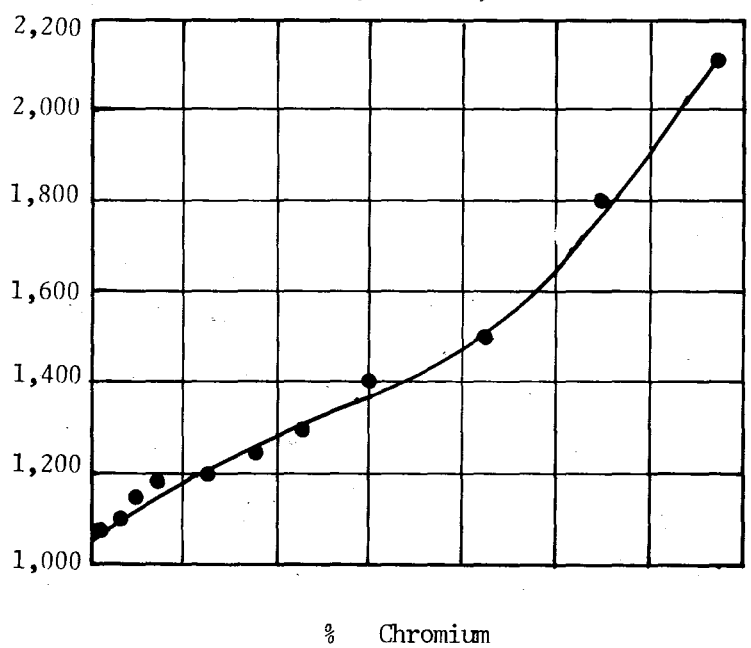

Figure 7. Effect of chromium on the oxidation resistance of steel in a normal combustion atmosphere. (After Krebs, Ref. 20)

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