Diffusion Coatings for Corrosion Resistant Components in Coal Gasification Systems

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ABSTRACT

Heat-exchangers, filters, turbines, and other components in integrated coal gasification combined cycle system must withstand demanding conditions of high temperatures and pressure differentials. Under the highly sulfiding conditions of the high temperature coal gas, the performance of components degrade significantly with time unless expensive high alloy materials are used. Deposition of a suitable coating on a low cost alloy may improve is resistance to such sulfidation attack and decrease capital and operating costs. A review of the literature indicates that the corrosion reaction is the competition between oxidation and sulfidation reactions. The Fe- and Ni-based high-temperature alloys are susceptible to sulfidation attack unless they are fortified with high levels of Cr, Al, and Si. To impart corrosion resistance, these elements need not be in the bulk of the alloy and need only be present at the surface layers.

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EXECUTIVE SUMMARY

Advanced coal gasification systems such as integrated coal gasification combined cycle (IGCC) processes offer many advantages over conventional pulverized coal combustors. Heat-exchangers, filters, turbines, and other components in coal-fired power plants are often must withstand demanding conditions of high temperatures and pressure differentials. These components are exposed to corrosive gases and particulates that can erode the material and degrade their performance. In collaboration with U.S. Department of Energy and Conoco/Phillips, we are developing corrosion-resistant coatings for high temperature components in IGCC systems. To help select the appropriate substrate and coating materials, we conducted a brief review of the different environments that the components may be exposed to, the alloy materials that are commonly used, and the coating technologies.

Coal is a complex and heterogeneous substance that contains several impurities including sulfur, chlorine, nitrogen, and metal compounds. During gasification many of these impurities are converted to gaseous species such as H_2S, HCl, NH_3, $NaCl$, and AsH_3. If coatings are to be used to provide corrosion resistance their compositions must be chosen appropriately to protect the components under gasifier conditions. Although the actual gas composition depends on the gasifier design and the type of coal that is being used, it generally has a low $p(O_2)$ and a high $p(S_2)$, in contrast to high $p(O_2)$ prevalent in many high temperature furnaces and gas turbines. The conditions in a gasifier stream are highly sulfiding in nature and require development of novel coating techniques to impart adequate corrosion resistance.

The selection of the substrate material is generally governed by the service temperature, stresses that the structures are likely to experience, erosion and corrosion resistance, and cost. For high-temperature applications, the components tend to be made of high-alloy steels that contain Fe, Cr, Ni, Co, and other elements to provide sufficient mechanical strength at the temperature of operation. The results described in the published literature indicate that many ferrous materials suffered breakaway corrosion in coal gasification atmospheres. High nickel alloys are more susceptible to sulfidation attack due to formation of $Ni-Ni_3S_2$ eutectic that melts at 635°C. Increasing Cr content to levels greater than 25 wt% in Fe-Cr-Ni alloys is generally effective against sulfidation corrosion. Addition of Al and Co appears to improve the sulfidation resistance. Other beneficial elements include Ti and Si. We postulate that the formation of a stable barrier containing Al_2O_3, SiO_2, or TiO_2 are partly responsible for increased corrosion resistance.

Even under conditions where the Cr_2O_3 is stable, sulfidation attack is feasible. The alloying element that forms a stable sulfide can diffuse through the oxide scale and eventually form sulfide on the surface of the oxide scale, leading to breakaway corrosion. Conversely, sulfur may migrate along grain boundaries and disrupt the protective layer. A diffusion barrier layer may be needed to prevent this type of corrosion. Thin layers of Si or SiO_2 deposited on an Fe-Cr alloy improved corrosion resistance against sulfidation at about 700°C, due to the presence of a SiO_2 layer at the alloy surface that acts a barrier to the migration of sulfur inward and cation transport outward

In summary, information available in the literature shows the corrosion reaction is the competition between oxidation and sulfidation reactions. The Fe- and Ni-based high-temperature alloys are susceptible to sulfidation attack unless they are fortified with high levels of Cr, Al, and Si. To impart corrosion resistance, these elements need not be in the bulk of the alloy and need only be present at the surface layers.

INTRODUCTION

Advanced coal gasification systems such as integrated coal gasification combined cycle (IGCC) processes offer many advantages over conventional pulverized coal combustors. IGCC systems have high energy-conversion efficiencies, reduced pollutant emissions, modular construction, and potentially low capital and operating costs. The gasification process allows the contaminants to be removed in their reduced or reactive state. The volume of a coal gas stream is less than that of a combustor flue gas stream in a plant of comparable size; hence, capital and operating costs for contaminant removal are less. Fixed-, fluidized-, and entrained-bed reactors have been developed and tested for coal gasification.

Heat-exchangers, filters, turbines, and other components in coal-fired power plants are often have to withstand demanding conditions of high temperatures and pressure differentials. Further, the components are exposed to corrosive gases and particulates that can erode the material and degrade their performance. In collaboration with U.S. Department of Energy and Conoco/Phillips, SRI International recently embarked on a project to develop corrosion-resistant coatings for coal-fired power plant applications. Specifically, we are seeking to develop coatings that would prevent the corrosion in the tube-sheet of the high temperature heat recovery unit of a coal gasification power plant operated by Wabash River Energy Laboratory (WREL) in Terre Haute, IN. This corrosion is the leading cause of the unscheduled downtime at the plant, and hence success in this project will directly impact the plant availability and its operating costs. Coatings that are successfully developed for this application will find use in similar situation in other coal-fired power plants. To help select the appropriate substrate and coating materials, we conducted a brief review of the different environments that the components may be exposed to, the substrate materials that are commonly used, and the coating technologies.

DEGRADATION OF MATERIALS IN COAL GASIFICATION SYSTEMS

Coal is a complex and heterogeneous substance that contains several impurities including sulfur, chlorine, nitrogen, and metal compounds. During gasification many of these impurities are converted to gaseous species such as H_2S, HCl, NH_3, NaCl, and AsH_3. The gas streams from fixed-, fluidized-, and entrained-bed coal gasifiers have different compositions and temperatures (Table 1).

Table 1

Characteristics of Gas Streams from Various Coal Gasifiers

System Characteristics	Fixed-Bed Gasification	Fluidized-Bed Gasification	Entrained-Bed Gasification
Process	Lurgi	KRW	Texaco
Exit Temperature (°C)	450-600	700-1000	1300
Pressure (psig)	300	300	450
Oxygen Potential	Reducing	Reducing	Reducing
GasComposition(%)			
CH_4	4.28	4.5	0.3
C_2H_4	0.13	<0.01	<0.01
C_2H_6	0.20	<0.01	<0.01
H_2	20.92	30.0	29.8
CO	7.49	45.0	41.0
CO_2	15.28	9.0	10.2
H_2S	0.6-1.1	1.1	1.0
COS	0.03-0.06	0.1	0.1
N_2/Ar	0.18	0.8	0.8
NH_3	0.4	0.2	0.2
H_2O	50.5	9.5	17.1
Particulate Loading (ppm)	1000-2000	1000-10,000	4000

The extent to which the materials undergo corrosion is influenced by the prevailing chemistry, temperature, and other parameters. In coal gasification systems, the gasification of coal occurs at high temperatures by reaction of controlled levels of oxygen and steam with coal and the resulting gas environment is reducing. In contrast to the gaseous environment in coal combustors is oxidizing in nature. For example, the sulfur in coal is converted into SO_2 in a coal combustor or H_2S in a coal gasifier. In general, H_2S is more reactive than SO_2 and when it is present at high levels metal surfaces are converted into corresponding sulfides. The sulfides do not form protective coatings and the metal underneath the sulfide layer continue to be attacked.

Coating materials must therefore be chosen appropriately to provide the right kind of protection. Although the actual gas composition depends on the gasifier design and the type of coal that is being used, it generally has a low $p(O_2)$ and a high $p(S_2)$. The gas, using a typical coal from an O_2-blown gasifier such as the one operating at WREL, may contain 28% H_2, 36% CO, 13% CO_2, 15% H_2O, 1% CH_4, 2% Ar and N_2 and up to about 2% H_2S. The $p(O_2)$ and $p(S_2)$ of this gas are about 10^{-15} atm and up to 10^{-4} atm, respectively at 870°C. These conditions are

highly sulfiding in nature and require development of novel coating techniques to impart adequate corrosion resistance.

Other components of the gas stream from the coal gasifier may also cause corrosion. The gas stream from a fixed-bed gasifier such as Lurgi is at a relatively low temperature of about 550°C and contains a significant fraction of hydrocarbons (including tars), and a low level of CO. The gas stream from an entrained-bed, slagging gasifier such as Texaco oxygen-blown gasifier is at a temperature of 900° to 1100°C, contains relatively little hydrocarbons, and has a high level of CO. The partial pressure of NH_3 is higher in the gas stream from a fixed-bed gasifier than that from fluidized- and entrained-bed gasifiers. The particulate matter is low in the fixed-bed design compared to that in the other two types of gasifiers.

The hot reducing gas leaving a slagging gasifier is typically at temperatures exceeding 900°C, and heat exchangers or syngas coolers are used to recover most of the sensible heat in the coal gas. The reducing environment also leads to the presence of alkali vapors in the gas stream, which are also very corrosive due to interaction with the protective oxide layers present in a heat exchanger surface.

In addition to the direct chemical attack by the gaseous components, the particulate matter present in the gas stream of a coal gasifier can also attack ceramic components or protective oxide surfaces of alloy steels. A fraction of the mineral matter in coal escapes the gasifier or combustor in the form of flyash. The composition of flyash depends on the type of coal, and combustion or gasification conditions and the particle size of the ash. A subpilot scale test conducted by Westinghouse Science and Technology Center with cross-flow filters at the Texaco pilot-scale gasifier facility at Montebello showed a particulate loading to the filter varied from 250 to 2000 ppm [Lippert et al., 1991]. A similar testing at the PFBC facility of New York University indicated that the cross-flow filter was able to reduce to ash dust loading from an inlet level of 250 to 1050 ppm to about 3 to 30 ppm [Lippert et al., 1989]. Thus, although the high temperature barrier filters are able to remove nearly 99% of the flyash, a small amount escape the filters and these particles (likely to be submicron fume) could be reactive because of their relatively high surface area and intimate contact with the of alloy steel components. The constituents of these particles are silica, silicates, alumino-silicates, ferrous oxides, alkali and alkaline earth compounds. The alkali compounds especially are likely to react with system components, forming chemical phases that are weaker or otherwise corroded. Table 2 lists the predicted phases to be formed by the interaction of flyash components with the surfaces of alloy steels.

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Table 2

Thermodynamically Projected Solid Phases Formed between Ash and Alloy Steel Surfaces

	Oxide Layer on the Alloy Steel Surface			
Ash Component	Fe_2O_3	NiO	Cr_2O_3	Al_2O_3
SiO_2	Iron silicates	Nickel silicate	Mixed oxides	Aluminosilicates
Al_2O_3	Iron aluminate	Nickel aluminate	No interaction	-
CaO	No interaction	No interaction	Calcium chromate	Calcium aluminate
MgO	No interaction	No interaction	Magnesium chromate	Magnesium aluminate
Na_2O	Sodium ferrite	No interaction	Sodium chromate	Sodium aluminate
K_2O	Potassium ferrite	No interaction	Potassium chromate	Potassium aluminate
Fe_2O_3	-	No interaction	Iron chromate	Iron aluminate

The composition of the submicron fume that is most likely to escape the barrier filters differs significantly from that of the coarser particles retained by cyclones and barrier filters [Quann et al., 1990]. Oxides of Si, Al, Mg, Fe, and Ca are generally the major constituents of the fume. Several other compounds of Na, P, Mn, V, Cr, As, Sb, Zn, Co, and Ba can also be present. The compounds of Na, P, As, and Co are significantly enriched in the fume fraction in comparison the coarser particles. The major oxides and alkali compounds pose a significant threat to the stability of protective oxides present in alloy steels used in a gasifier system.

By depositing on the heat exchanger tubes, particulate matter in the gas stream degrades their performance. However, at high flow velocities they can also have a detrimental effect by eroding the protective coating. Natesan (1993) has reviewed the temperature and chemical environments experienced by heat exchangers and turbines under various coal-utilizing technologies. He has also reported on the mechanisms and failure modes experienced in these components (Tables 3 and 4).

Liquid water is another factor in causing corrosion. Although under most operating conditions, water will be in the vapor phase, during shutdown and startup periods the steam can condense and form pools in contact with the component materials. Liquid water could dissolve certain salts and contact of metal surfaces with this salt solution can lead to pitting corrosion.

Table 3. Service conditions and modes of degradation for component materials in coal-fired systems						
Component System	Gas Environment.	Gas Temp. Range (°C)	Metal Temp Range (°C)	Deposit Type	Particulate and/or Particle Velocity	Mode of Degradation
Heat Exchangers						
PC boilers	Oxidizing	1300-1600	400-700	Alkali Sulfates Ash	Fly ash, < 20 m/s	Alkali corrosion Fouling
FBC	Oxidizing, locally reducing	850	400-850	$CaSO_4$, CaO Carbon, Fly ash Fly ash	Sorbent bed, fly ash 3-? m/s	Oxidation/Sulfidation Erosion
IGCC	Reducing, moderate to high H_2S	900-1100	400-650	Fly ash Alkalis Chlorides	Fly ash, < 20 m/s	Sulfidation/erosion? Fouling
HIPPS	Oxidizing	1300-1600	400-1300	Fly ash, Slag Alkali sulfates	Fly ash	Ceramic fracture Alkali corrosion Fouling
LEBS	Reducing, Sulfidizing	1300-1600	400-600	Sulfides Slag	Fly ash	Sulfidation Deposit corrosion Fouling
Turbines						
IGCC	Oxidizing	850-900	850-950	Fly ash/slag Alkali	Slag, 200-500 m/s	Hot corrosion/erosion
FBC Effluent	Oxidizing	850-900	600-900	Alkali sulfates Silicates Sorbent	Fly ash, sorbent, 200-500 m/s	Hot corrosion/erosion
HIPPS	Oxidizing	1300	1000	Alkalis	200-500 m/s	Oxidation/erosion

Source: Natesan,, 2001

Table 4. Materials degradation in coal-fired systems		
Phenomenon	Key Variables	Possible Rate-Limiting Step
Boiler tube corrosion	Alkali and chlorine contents Fly ash, temperature	Alkali condensation Oxide-sulfate reaction
Substoichiometric combustion (also gasification)	O and S partial pressures, temperature Downtime condensate Alkali/slag deposit	Fracture of oxide scale Oxidation/sulfidation Pitting and crevice corrosion
FBC in-bed corrosion	Bed chemistry Local particle velocity Particle size and loading	Oxidation/sulfidation Arrival rate of particles Fracture of surface scales
Low-temperature hot corrosion	Temperature, temperature gradient salt-film thickness, S and alkali level	Sulfidation of transient oxides Transport of base metal (e.g., Ni and Co)
Hot corrosion/erosion	Alkali level Temperature Particle size, loading, and velocity	Fracture of scale Sulfidation of transient oxides Transport of base metals

Source: Natesan, 2001

COMPONENT MATERIALS

The selection of the substrate material is generally governed by the service temperature, pressure differentials (stresses) that the structures are likely to experience, erosion and corrosion resistance, and cost. For high-temperature applications, the substrates tend to be high-alloy steels that contain Fe, Cr, Ni, Co, and other elements to provide mechanical strength at the temperature of operation. Even the ability of alloy steels to withstand high stresses decreases sharply at elevated temperatures. Figures 1 and 2 present data on the ranges of conditions under which different alloys are useful as substrate materials [Viswanathan, et al., 2003]. It shows that the strength of the ferritic materials declines rapidly above 600°C.
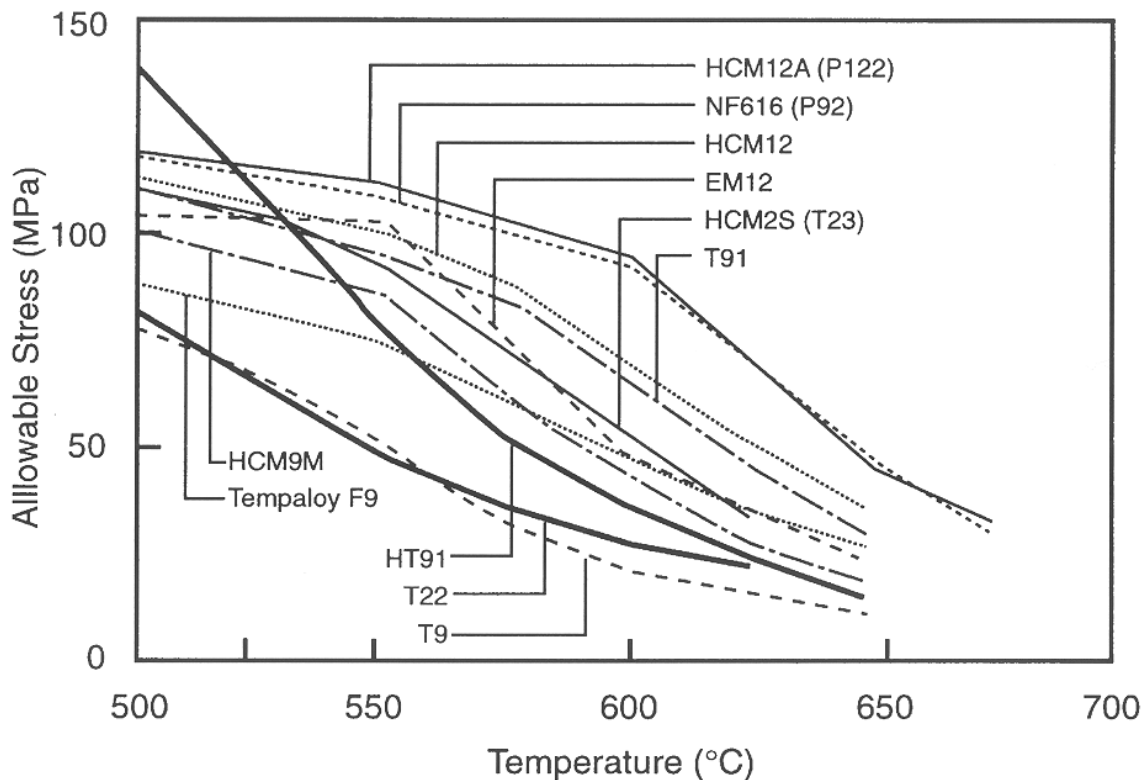
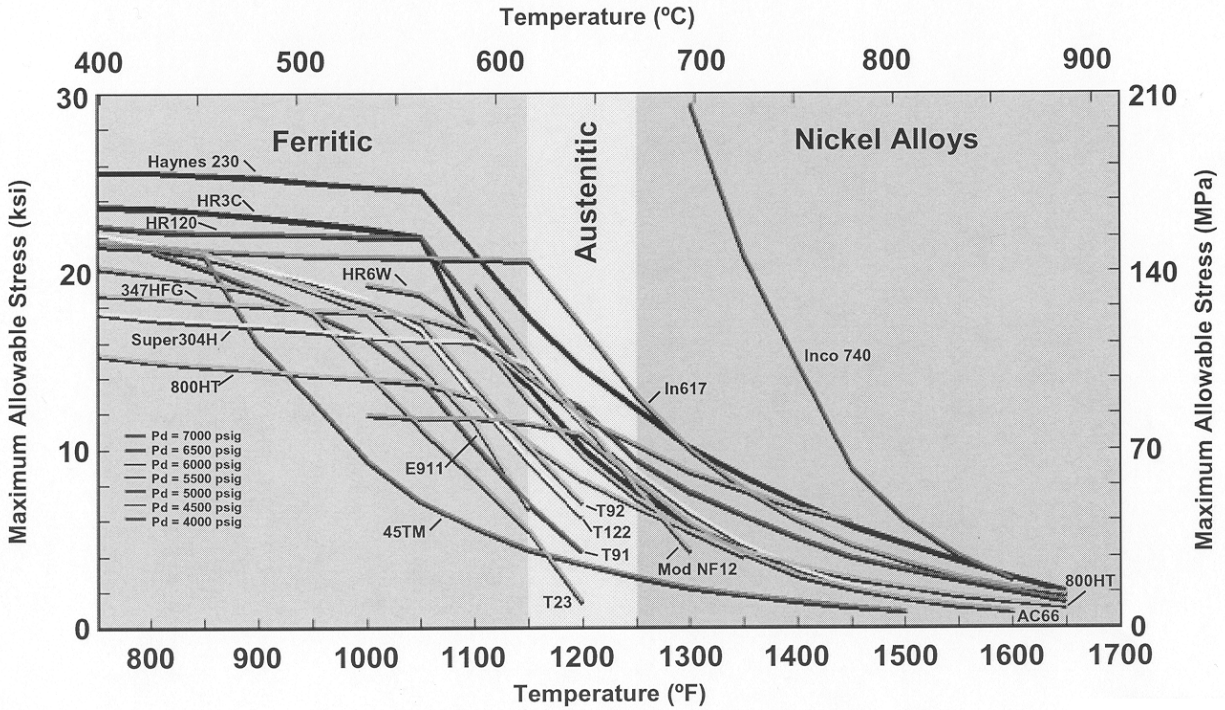Figure 1. Allowable stress of various alloys as a function of temperature.

Figure 2. Maximum allowable stress of alloys as a function of temperature.

A second selection criterion of a component material is its ability to resist corrosion or oxidation during service. In general, alloy steels depend on the formation of a protective oxide layer such as Cr_2O_3 for protection against sulfidation or further oxidation. Although Cr_2O_3 scale is generally protective against sulfidation, high levels of H_2S may cause sulfidation even of Cr_2O_3 in gasifiers operating in O_2-blown mode with moderate to high sulfur coals.

Many studies have been conducted on the degradation of metal alloys in coal gasification atmospheres [Humphreys and Schafer, 1983]. Several alloys suffered breakaway corrosion under such conditions. High nickel alloys are more susceptible to sulfidation attack due to formation of Ni-Ni_3S_2 eutectic that melts at 635°C. Increasing Cr content to levels greater than 25 wt% in Fe-Cr-Ni alloys is generally effective against sulfidation corrosion. Co-containing alloys are also more resistant to sulfidation than Ni-based alloys. Verma suggested that Cr_2O_3 scale doped with Co improves sulfidation resistance.[Verma, 1982] Addition of Al also improves the sulfidation resistance [Bradshaw, 1977]. Recently, iron aluminides have been tested in coal gas environments and are found to be superior to high-Cr alloys [Natesan, 2001]. Other beneficial elements include Ti and Si. A Ni-Co-based alloy (HR-160) developed by Haynes International containing high Cr and Si is claimed to have exceptional sulfidation resistance [Lai, 1990]. We postulate that in the above cases, the formation of a stable barrier containing Al_2O_3, SiO_2, or TiO_2 are partly responsible for increased corrosion resistance.

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Even under conditions where the Cr_2O_3 is stable, sulfidation attack is feasible. The alloying element that forms a stable sulfide can diffuse through the oxide scale and eventually form sulfide on the surface of the oxide scale, leading to breakaway corrosion. According to a mechanism, alloying elements such as Mn, Fe, Co, and Ni diffuse through the Cr_2O_3 scale and react with H_2S on the top of the oxide scale to form an external sulfide scale [Perkins et al., 1982]. Mn is the fastest diffusing element, followed by Fe, Co, Ni, and Cr. Alternatively, the corrosion mechanism may involve penetration of S atoms through the oxide layer to form discrete particles of sulfides in the base alloy matrix. A diffusion barrier layer may be needed to prevent this type of corrosion.

COATINGS

Natesan (1993) reviewed the suitability of Al, Cr, and Si coatings made by pack cementation, electrospark deposition, plasma spray, and CVD for coal gasification and combustion applications. A minimum Cr concentration of 25 wt% or an Al concentration of 15 wt% is required to achieve adequate sulfidation resistance at about 650°C. Addition of V to the Cr layer minimized the formation of chromium carbides at the grain boundaries. These studies indicated that increased Cr and/or Al levels in the alloy is beneficial in resisting sulfidation attack, but the integrity of the coating is strongly dictated by the adhesion of the coating to the substrate. Thin layers of Si or SiO_2 deposited on an Fe-Cr alloy improved corrosion resistance against sulfidation at about 700°C, due to the presence of a SiO_2 layer at the alloy surface that acts a barrier to the migration of sulfur inward and cation transport outward.

CONCLUSIONS

In summary, information available in the literature shows the corrosion reaction is the competition between oxidation and sulfidation reactions. The Fe- and Ni-based high-temperature alloys are susceptible to sulfidation attack unless they are fortified with high levels of Cr, Al, and Si. To impart corrosion resistance, these elements need not be in the bulk of the alloy and need only be present at the surface layers.

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