FAILURES OF METALS IN SULPHUR AND SULPHUR BEARING MEDIA

By

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ABSTRACT

Failure of metal components which occur in media containing sulphur and sulphur-bearing compounds are attributed to the corrosive action of sulphurous gases acting on porous metal surface scale and actuating intergranular failure. Other important influences are of moisture, aeration, temperature and mechanical stresses. These factors have been discussed in outline, illustrated with examples of actual service failures. The paper is concluded with remedial measures such as metallizing with chromium, aluminium etc., besides considering substitute metals for use in sulphur atmospheres.

INTRODUCTION

Sulphur and its compounds rank next to oxygen in their wide prevalence and chemical reactivity to metals. They find extensive applications in the manufacture of adhesives, in sulphite pulp plants, in paper industry, in pickling and plating solutions, in petroleum refineries and in a number of chemical industries. Gaseous sulphur compounds are widely encountered during roasting and smelting operations relating to the extraction of non-ferrous metals from sulphide ores. They are often present in furnace atmospheres and exercise highly deleterious effects on different metals and alloys¹, (Figs. 1, 2 and 3). Considerable work has been done regarding the analysis of injurious effects of sulphur and its compounds on different types of alloys and in its wake new alloys have been successfully developed to withstand sulphur corrosion. Yet failures directly attributed to sulphur and sulphurous compounds are not uncommon.

Mechanism of Sulphur Corrosion and Failure:

The mechanism of attack of metal components exposed to sulphurous media, proceeds basically with the penetration of sulphur into the metal surface and grain boundaries on the principle of counter current diffusion and chemical interaction ${}^2,{}^3$. Whereas sulphur atoms tend to diffuse inwards, the metal atoms try to migrate to the surface through the scale. Scale formation is an essential pre-requisite to this diffusion process. In a homogenous atmosphere, the rate of diffusion in a binary system is governed by the relation

$$\frac{\mathrm{dw}}{\mathrm{dt}} = -D. \ \mathrm{dc/dx}$$

where D is the diffusion constant and dc/dx is the concentration gradient of the diffusing element or compound.

Value of the diffusion constant D depends mainly on two factors viz., (1) Nature of the element or compound diffusing through (2) Chemical, physical and structural characteristics of the metal medium and its surface scale through which diffusion takes place. If the surface scale is porous, diffusion of sulphur is accelerated, and if it is compact and impervious, diffusion process is retarded.



FIG. 1. S.A.E. 1015 Steel, Heated at 2000°F, 60 minutes. 0.2% sulphur dioxide; complete combustion of city gas and air. x 500 unetched.
S.A.E. 1015 steel, heated at 2300°F, 40 minutes shows oxide-sulphide cutectic x 750 unetched. (Murphy D.W.¹)



FIG. 2. S.A.E. Steel, heated 40 minutes in atmosphere of complete combustion of city gas—air mixture containing 0.2% sulphur dioxide at 2450°F, showing the severity of attack by sulphur-bearing atmosphere at high temperature x 100 unetched.

S.A.E. 1015 Steel at 2300°F heated for 40 minutes in an atmosphere of complete combustion of city gas-air mixture containing 0.2% sulphur dioxide, showing globular inclusions at the edge. Unetched x 100. (Murphy D.W.¹)



 FIG. 3. S.A.E. 1015 Steel heated at 2300°F., 120 minutes in an åtmosphere of complete combustion of city gas-air mixture containing 0.2% sulphur dioxide showing the penetration of inclusions.

S.A.E. 2320 Steel heated 40 minutes at 2300 F., in an atmosphere of combustion of city gas-air mixture containing 0.2% sulphur dioxide, showing the severe attack sustained by nickel-bearing steel in sulphurbearing atmosphere at forging temperature. Unetched x 100. (Murphy D.W.¹) Concentration gradient dc/dx depends upon the solubility of element or compound diffusing into the medium and the latter's depth through which diffusion occurs.

In actual practice the mechanism is not however so simple but is highly complicated due to heterogeneous conditions. The process is therefore dependent upon a number of factors in common with all diffusion phenomena, but the most important are that of temperature, oxygen, alloying elements, water vapour and mechanical stresses. ^{4'3'6'7'8'9'10'11'12'13'14} In general, scaling is greatest, when two or more phases are formed by interaction and when these phases react with each other. In ferrous materials for instance, in presence of oxygen at elevated temperatures, FeO—FeS eutectic of low melting point (2000°F) is formed and this is highly soluble in the parent metal. Its diffusion is thus greatly accelerated and the resulting attack at the grain boundaries causes failure through intergranular embrittlement and disintegration. Although majority of service failures are caused by this diffusion or sulphur into the grain boundaries (Fig. 4), other causes also operate thereto.

Nickel-chrome and chrome stainless steels: These steels are embrittled under certain service conditions due to intergranular corrosion caused by the loss of their passivity characteristics. Oxidation passivity is conferred by chromium on its alloys and sulphurous gases adversely affect this 15³16³17³18³19³20³21</sup> passivity particularly in reducing atmospheres and in steels of low chromium contents (Figs. 5, 6, 7 and 8).

Nickel and High Nickel Alloys: Sulphur and its compounds react strongly with nickel forming nickel sulphide with which nickel forms a cutectic series of alloys, the cutectic temperature being $1191^{\circ}F^{22}$. The penetration of sulphur in nickel and nickel steels is therefore pronounced due to the influence of nickel in increasing the solubility of sulphur in steel. Nickel offers, therefore, very little resitance to sulphur atmospheres and failure chiefly takes place through intercrystalline embrittlement (Figs. 9 and 10). Even contamination of nickel with sulphur results in intense pitting.

Cast Iron: The phenomenon of failure ^{23'24} of cast iron parts when exposed to sulphur media takes place by bursting and fissuring around the graphite lamellae caused by the interaction of sulphur tri-oxide with silicon containd in the iron forming silica. Thermal grain growth and volume changes accelerate the pace of sulphur attack.

The injurious effects of sulphur contained in furnace gases have also manifested themselves through loss of mechanical strength in case of quality steels and their total collapse in service. In other cases, failures have been traced to the formation of sulphur acids and their corroding and dissolving effects on metal surfaces.

Practical Service Failures :

Corrosion effects at high temperatures due to sulphur compounds are no where so acutely felt as in non-ferrous smelteries during roasting and smelting operations²⁵. By far the largest number of failures are encountered in metal components used for ore roaster parts hot calcine bins, reverberatory furance and convertor parts etc. The corrosive constituents are chiefly sulphur dioxide, sulphur tri-oxide and free sulphur. Many parts of roaster units are directly exposed to such corrosive media during matte roasting of the copper sulphide concentrates and dead roasting of galena and sphalerite. The parts affected are chiefly rabble arms, shoes and blades in a multiple reverberatory roaster. In a Dwight-Lloyd roaster, the parts affected are pallets, grate bars, members of the suction box assembly and the track circuit. Roasting conditions demand excess of air at a high temperature where the affinity of oxygen for sulphur is greater than for the metal resulting in maximum formation of sulphur dioxide and a minimum of sulphur trioxide. Any sulphur trioxide formed combines with some of the metallic oxides to form sulphates. For such drastic service requirements entailing high temperature strength and resistance to sulphur compounds, special alloys have been evolved. For rabble arms and blades, 22-25% chromium-iron alloy castings with 1—1.25% carbon are preferred to those containing 16-18% chromium with .75 to 1% carbon. Brown²⁵ has reported that in some plants chromium-iron rabble arms and blades have given a life of 800-1200 days as compared to normal life of 250-400 days for a plain cast iron or carbon steel component under identical service conditions.



FIG. 4. Section of Scale formed on 0.13% carbon steel in neutral atmosphere 0.20% S0₂ at 1000°C for 8 hrs. Section (b) shows eutectic along grain boundaries and section (c) structure of eutectic. (Reduced to four-fifth linear in reproduction). (Cobb et al¹⁴).



FIG. 5. Chrome-nickel heating spiral. Scale formation due to sulphur penetration. 9/10 of natural size. (Gruber, H,¹⁰).

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FIG. 6. Photo of a section of a chrome-nickel heating spiral. Cracks due to sulphur attack. Unetched. (Gruber, H¹⁰)



FIG. 7. Chrome-Nickel. Gaseous sulphur at ack. Etched, (Gruber, H¹⁰).



FIG. 8. Chrome-Nickel. Nickel sulfide attack (boundary zone). Unetched. (Gruber, $H^{10}).$



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FIG. 10. Nickel becomes brittle due to penetration of sulphurous acids Left : heated in nitrogen Right : heated in sulphurous acids.

Bins or Hoppers for the Hot Calcines:

Hot calcines from a multiple reverberatory roaster are usually stored in large bins before smelting. Temperature of the calcines as received from the roaster, is of the order of 1200-1400°F. Material used for these bins should therefore be able to resist oxidation, chemical corrosion and heat besides possessing good mechanical properties at elevated temperatures. Carbon steel plates were first used which failed badly due to oxidation. These were replaced by nickle-chromium steels, one of 18-8 composition and another of 24% chromium with 11% nickel. Both these steels showed little or no deterioration even after two years of continued service.

In the manufacture of sulphuric acid from flue gases obtained during roasting of sulphide ores, equally severe corrosive conditions prevail. Sheet iron or boiler plate steel initially employed for flue parts failed badly through corrosion of hot oxidizing sulphurous gases accelerated by the presence of moisture. Smelteries had therefore to resort to concrete or brickflue construction and subsequently to corrosion and heat resistant steels.

Failures in chemical industry:26

The chief cause of failure of metal components used in chemical industry is due to lack of resistance to acid corrosion. Moisture present in the atmosphere or resulting from condensation processes acts as a catalyst for the formation of sulphuric acid. In Contact plant used in the manufacture of sulphuric acid, certain parts are exposed to the combined influence of temperature and contact with sulphur trioxide and sulphuric acid. Steel tubes of the heat exchanger plant, wherein heat is transferred from hot gases from converters to cold mixture of sulphur dioxide and air on its way to the contact mass, are reported frequently to fail due to acid corrosion. These exchanger tubes which are usually made of cold drawn seamless steel tubing, resist well the action of dry sulphur trioxide and sulphuric acid in both hot and cold conditions, but failed when they were moist due to inadequate drying.

Failures in Petroleum Refineries:27,28

Whilst acid corrosion is the principal cause of failures in chemical industries, the problem facing petroleum refineries is that of sulphide corrosion. Parts of refinery equipment chiefly affected are, valves and fittings, charging stocks, and cracking coils of the pressure still equipment. In many cases, addition of suitable neutralizers to crude oils containing corrosive sulphides, had a beneficial effect in minimising corrosion damage.

Failures of Ferrous Materials:

Honeyman and Fisher²⁹ experienced an interesting case of failure of a mild steel tube when it was heated to 1650°F. for bending. For preventing its collapse during bedning it was packed with powdered sand and given an insertion of a thin sheet of metal and plugged thereafter. After heating, a hole was found at an isolated portion through the sheet insert, besides a cavity in the tube. Microstructure of the steel at the base of the cavity revealed the presence of FeO-FeS eutectic (Fig. 11). The contamination of sulphur had evidently occured from the sand used.

In forging of steel, suitable selection of fuel is important. It should be free of sulphur to prevent contamination of steel. Cases have been observed where the use of inferior sulphur bearing coals have not infrequently led to disintegration of the steel in the forge through the formation of FeO-FeS eutectic.

Talbot and Skinner³⁰ have also attributed severe embrittlement of heat-resisting alloys containing high nickel to sulphur contamination from low grade heavy oil or pulverised coals used for heating purposes.

Failures of Nickel and Nickel-Base Alloys:

Failures in nickel alloys are mainly due to sulphidising embrittlement. In one instance³¹, Monel metal component used in hydrogen sulphide gas running at 1000°F. failed only after 6 weeks' service through severe intergranular embrittlement. In another case, pure sulphur dioxide at 1292°F. was found to be about 20 times more damaging to Monel than oxygen. It is



Fig. 11. Shows a longitudinal section through the wall of the tube and the micro-structure of the steel at the base of the cavity. This is the Fe0-FeS eutectic. (Honeyman and Fisher²⁹).

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therefore essential that in heating of nickel-copper alloys for forging or annealing, sulphur bearing gases should be eliminated in furnace atmospheres since exposure even for a short period results in severe embritlement. In another casse, marking on a nickel piece with a chalk contaminated with sulphur compounds resulted in its cracking on subsequent heating. A nickel wire when heated whilst embedded in asbestos packing which happened to carry sulphur compounds was found to be severely embrittled. In these cases, decomposition of sulphur compounds present in the materials used in the operation during heating, is the cause of embrittlement.

Metals and Alloys Suitable for Resisting Corrosive Effects of Sulphur and its Compounds:

A number of alloys are available to withstand the corrosive effect of sulphur and its compounds. A judicious selection is necessary in choosing them depending upon the nature of the media to be encountered, their concentration, atmospheric environments etc.

Aluminium : Aluminium is not attacked by sulphur in liquid or vapour form. Aluminium freight cars have been used to transport sulphur and sulphur bearing coal and ores without any detrimental effect. Greater use is visualised for this metal for pipe lines and railroad cars used for handling sulphur. However, its low melting point puts limitations to its use at higher temperatures.

Magnesium : Magnesium offers excellent resistance to molten sulphur and is inert to liquid and gaseous phases. Its chief drawback is low melting point and high cost.

Manganese: Upto temperatures of 750°F manganese resists well the attack of sulphur and possesses enhanced resistive power when alloyed with certain other metals.

Chromium : Of all elements, it is chromium that displays greatest resistance to attack by sulphur and its compounds through its unique property of surface passivity.

Sulphur Resistant Alloys:

Nickel-chromium and chromium stainless steels: These alloys are foremost in service in view of their resistance to corrosion, oxidation and heat.

Conventional stainless compositions resist liquid sulphur upto 400°F. For handling liquid sulphur upto its boiling point, 17% chromium steel or stabilised 18-8 stainless steel gives satisfactory service. For operations involving sulphur in vapour form at temperatures upto 1300°F., 25-20 chrome-nickel alloy, 27% straight chromium steel, and alloys containing 27 chromium and 2 to 3% aluminium have given satisfactory service performance. High chromium steels are preferred to chrome-nickel steels and chromium-aluminium steels to straight-chromium steels for these purposes. For general service however, nickel-chromium and chromium-iron alloys are employed with about 12% or more of chromium. 20-30% is perhaps the best limit for chromium to offer good resistance to sulphur corrosion and if nickel is present, chromium should be atleast 25% to withstand the severe operational conditions. In oil industry, the use of 24% chromium and 12% nickel alloy steels are greatly preferred. These alloys offer no casting difficulty and need no heat-treatment.

Complex Alloys:

Additions of molybdenum to chromium steels and austenitic 18-8 chromium-nickel steels, greatly improve their resistance to sulphuric, sulphurous and organic acids, as molybdenum confers passivity besides strengthening the surface film. Molybdenum also forms a useful alloying element to nickel base alloys and commercial alloys have been developed to withstand the corrosive action of sulphuric acids over a wide range of temperature and concentration. Three such alloys are given below:

HASTELLOY 'A' (Hynes-Stellite Co., Indiana)

Composition: Ni-53%, Mo-22%, Fe-22%, Si-1%, Mn-2%, C-0.1%) Properties and uses: It withstands well the corrosive action of sulphuric acids over a wide range of temperature and concentrations upto 70% and is wear resistant. It is used for pump and valve castings used in sulphuric acid plants.

HASTELLOY 'C' (Haynes-Stellite Co., Indiana)

Composition: Ni=51%, Mo=19%, Fe=6%, Cr=17%, W=5%, Si=1%, Mn-1%, C=0.1%)

Properties and uses: It exhibits superior properties than 'A' and resists well the action of wet hydrogen sulphide, sulphur dioxide, and sulphur trioxide upto 158°F. It is used for agitator parts, heating coils, cooling coils, pump parts, valves etc.

HASTELLOY 'D' (Haynes-Stellite Co., Indiana)

Composition: Ni-85%, Al-3%, W-1%, Si-10%, Mn-1%, C-0.1% Properties and uses: This is yet another nickel base alloy which resists sulphuric acid at all concentrations and temperature upto the boiling point. It is recommended for equipment handling sulphuric acid, such as pumps, valve castings etc.

There are besides, a number of other compositions patented for use in sulphurous atmospheres. A few of them, with their trade name, properties and uses are described below:

1. RESISTAL KA2. (Crucible Steel Co. of America).

Composition : C-0.15%, Cr. 18.5%-Ni-8.5%, Fe-balance)

Properties and uses: This is a corrosion and heat-resistant alloy. It can be used in hydrogen sulphide atmospheres upto 1300°F and in sulphur dioxide atmospheres upto 300°F. It finds extensive applications in chemical plants and in oil refineries for cracking still tubes.

2. CYCLOPS NO. 17 (Cyclops Steel Co.)

Composition: C-0.4%, Si-1.00%, Mn-0.75%, Ni-20.0%, Cr 8.0%.

Properties and uses: Resistance to corrosion, abrasion at high temperatures are its chief characteristics. It can be used in sulphur dioxide atmospheres up to 1400°F. It is mainly used for valves, valve parts, turbine blades, thermocouple walls and miscellaneous refinery parts.

3. ENDURO A (Censral Alloy Steel Corporation)

Composition: C-0.10% max, Si-0.88%, Mn-0.50% max, Cr-17.5%.

Properties and uses: The alloy possesses corrosion and high temperature resistance. It can be used for components exposed to sulphur dioxide and sulphur trioxide atmospheres upto 1500°F.

4. MIDVALE H.R. (Midvale Company)

Compositon: C-0.35%, Mn-0.55%, Si-1.40%, Cr-19.50%, Ni-7.25%, W-4.0%.

Properties and uses. It is a corrosion and heat resistant alloy useful for service in hydrogen sulphide and sulphur dioxide atmospheres up to 1650°F. Recuperator parts, cast pyrometer tubes, furnace racks, high pressure and gas burner nozzles are usually made of this alloy.

5. CRALFER (Patented by British Cast Iron Research Association)

Composition: T.C.-3%, Mn-.6%, Si-1%, Cr-.75%, Al-7.25%.

Properties and uses. It is a heat resisting cast iron containing aluminium. It is resistant to scaling and growth and can be used in atmospheres containing sulphur upto 1700°F.

6. WORTHITE (Worthington Pump and Machinery Corporation, N.J.) Composition: Fe-48%, Ni-24%, Cr-19%, Mo-3%, C- .07% max, Si-3.5%

Properties and uses: It is resistant to acid corrosion especially in media containing sulphuric acid. For components such as pump parts, valves and other fittings used in sulphite pulp and paper industries and for parts operating in corrosive solutions containing sulphur dioxide with small amounts of sulphurous and sulphuric acid at 300°F., this alloy is reported to have given good service.

7. MONEL (Mond Nickel Co., Ltd., England)

Composition: Ni-66-67%, Cu-29-30%, Fe-.9 to 1.7%, Si-.05-.25%, Mn-0.4%, -1.1%, C-0.15% to 1%, Al-0.2%.

Properties and uses: It is a very versatile alloy for corrosion resistance in non-oxidizing acid medium like dilute sulphuric acid solutions. It also resists the embrittling effect of oil-well brines containing hydrogen sulphides and also dry sulphur dioxide at temperatures upto 600°F. It is used for rotary pulp washers, thickeners, and screens in sulphite pulp mills, and in pickling components exposed to 5% to 10% hot sulphuric acid solution.

A number of other processes can also be employed to confer resistance on metal surfaces to sulphur corrosion. Metallizing³² with elements known to be resistive to sulphur like A1, Cr, Mn, etc. may provide an adequate protective surface to the metal base. In one instance, boiler plate steel metalized with aluminium or chromium was found satisfactory upto 832°F against sulphur vapours. Plating³³, ³⁴ with chromium is reported to have successfully withstood the action of elemental sulphur and sulphide in both plain and aqueous solutions at various temperatures. Hot dipped aluminized steels are reported to give excellent service in industrial atmospheres con-taining sulphurous gases. In some cases³⁵, ³⁶, ³⁷ calorizing has given equally good service in furnace atmospheres containing hydrogen sulphide, sulphur dioxide, and sulphur trioxide. Calorized steel parts are widely accepted for use in equipment handling and refining crude oils, in Conttact sulphuric acid converter, etc.

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DISCUSSION

Dr. B.S. Nagraj:

Can a 45% solution of Ammonium sulphate at about 50 deg. C. have after long time any effect on 18/8 stainless steel stabilised with Titanium? Can that solution promote crystalline corrosion in the stainless steel mentioned ?

Dr. B.R. Nijhawan in reply stated that the performance of 18/8 steel under prolonged contact with hot ammonium sulphate solutions, will depend upon various factors e.g., the presence of residual stresses in the stainless steel structure which may give rise to "stress-corrosion" and "stress cracking" of the material causing its gradual failure, more likely through inter-granular breakdown in the initial stages. The authors would welcome undertaking actual investigations into failed 18-8 components under the above conditions of chemical service. It would be unwise to offer any off-hand definite comments at this stage.