WROUGHT AND CAST HEAT RESISTANT STAINLESS STEELS AND NICKEL ALLOYS FOR THE REFINING AND PETROCHEMICAL INDUSTRIES

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Wrought and cast heat-resistant stainless steels and nickel alloys for the refining and petrochemical industries

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A wide variety of iron and nickel-based materials are used for pressure vessels, piping, fittings, valves and other equipment in refineries and petrochemical plants. The most common of these is plain carbon steel. Although it is often used in applications up to 900-950ºF (482-516ºC), most of its use is limited to 600-650ºF (316-343ºC) due to loss of strength and susceptibility to oxidation and other forms of corrosion at higher temperature. Ferritic alloys, with additions consisting primarily of chromium (0.5-9%) and molybdenum (0.5-1%), are most commonly used at temperatures up to 1200ºF (650ºC). Their comparative cost, higher strength, oxidation and sulphidation resistance and, in some cases, their resistance to certain non-corrosive but debilitating environments (eg. hydrogen) result in their being the material of choice. However, these low alloys have inadequate corrosion resistance to many other elevated temperature environments for which more highly alloyed Ni-Cr-Fe alloys are required. Hydrogen-hydrogen sulphide and ammonia are two common examples of such environments.

For applications for which carbon or low alloy steels are not suitable, the most common choice of material is from within the 18 Cr-8Ni austenitic group of stainless steels. These alloys and the 18Cr-12Ni steels are favoured for their corrosion resistance in many environments and their oxidation resistance at temperatures up to 1500ºF (816ºC). Above 1200ºF (650ºC) their falling strength becomes a consideration and more heat resistant alloys must often be used.

There are many diverse applications for the stainless and heat resistant alloys throughout the range of temperature encountered in the refining and petrochemical industries. Some of the more important of those applications at temperatures below 1200ºF (650ºC) will be discussed because of their significance to the industries involved and to the use of these materials. However, the emphasis of this document is on applications of heat resistant alloys above 1200ºF (650ºC). Since there is almost no use of the chromium-iron or duplex stainless above 600ºF (316ºC), these alloys are not covered. A large percentage of the applications for stainless and heat resistant materials above 1200ºF (650ºC) are in connection with fired heaters. However, piping components, manifolds, valves, cyclones etc. also are constructed of these materials and are discussed. Applications for both wrought and cast versions of the heat resistant alloys are addressed. With rare exception, the latter are used commonly above 1500ºF (816ºC) and almost exclusively for applications above 1850ºF (1010ºC) up to 2100ºF (1150ºC).

Selection Criteria

Table I is a listing of the wrought stainless and heat resistant alloys most commonly used for refining and petrochemical plant equipment. *Table II* lists some of the newer wrought alloys and *Table III* the most commonly used cast alloys. Nominal compositions are included. The lists are not intended to be all inclusive but represent the largest volume of such alloys used.

The selection criteria used by the materials engineer in choosing from this group of materials includes a list of qualities that are either desirable or necessary. Unfortunately, the optimum properties associated with each selection criteria seldomly all occur in a single material, especially when the operating conditions become aggressive. Thus, compromises must frequently be made to realize the best performance of the material selected. The principle selection criteria applied to materials for refining and petrochemical plant equipment include, but are not necessarily limited to, the following:

- Mechanical properties;
- Corrosion resistance;
- Stability of properties;
- Fabricability;
- Availability;
- Cost.

Mechanical Properties

Most refining and petrochemical process equipment is designed and fabricated to the requirements of the American Society of Mechanical Engineers (ASME) or equivalent pressure vessel and piping codes of other countries. These codes include only approved materials and establish the basis for and the setting of allowable stresses. Thus, the mechanical properties of a material is usually the first criteria that the materials engineer applies in the selection process. This is especially important for applications at temperatures in the creep range where a minor difference in design/operating temperature can significantly affect the load carrying ability of the material. However, other applications may require that the component be able to support only itself. Obviously, in this case, criteria other than strength will take priority.

Tensile strength is the criteria used to select carbon and alloy steels for ASME Code applications below the creep temperature range. Some other codes rely on yield strength. Within the creep range, however, a limiting creep rate (eg. 1%/100,000hours) or a stress rupture life (eg. 100,000 hours) is usually the governing criteria. *Figure 1* represents one form in which stress rupture data are presented for use in material selection and component design. A more traditional format involves a log-log plot of stress vs. rupture time at different temperatures.
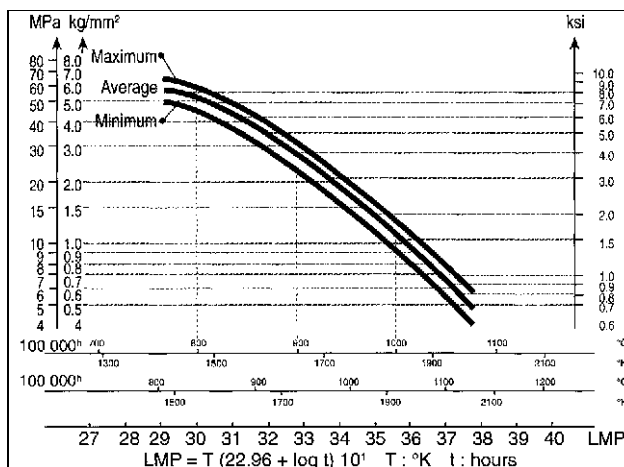

Figure 1 One manufacturer's format for presenting creep-rupture data for a centrifugally cast heat resistant HP-type alloy. (LMP = Larson-Miller Parameter). Source: Manoir Industries

Because applications for heat resistant alloys often involve frequent thermal cycling, their thermal fatigue resistance is an important mechanical property to consider in the selection process. This property is a function of composition but it is also affected by section thickness and geometry. An example of this relationship involves 180 degree return bends in ethylene cracking service. Some fitting designs include a heavy outside wall to absorb erosion from coke particles. These designs can suffer thermal fatigue as a result of the cyclic nature of regular operations, decoking, and startup and shutdowns. An example of the cracking that can result is shown in *Figure* 2. Thinner, uniform walled tubes and similar components experiencing the same magnitude and frequency of cycles did not develop this problem. Fortunately, through-wall cracking such as this occurs infrequently. It usually is arrested about midwall as the probable result of the crack acting as a hinge.
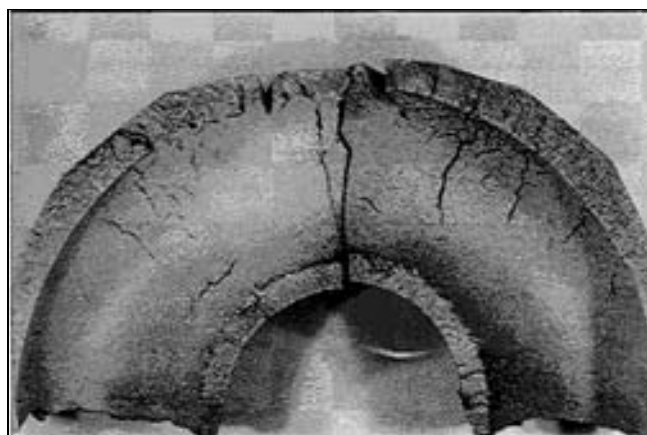

Figure 2 HP-type, statically cast return bend from the shield section of an ethylene cracking furnace after 4 years service. Through-wall cracks on heavy backwall are due to thermal fatigue

Table I   Established heat resistant alloys for refining/petrochemical applications, Nominal composition

Alloy	Cr	Ni	Fe	Co	C	Si	Mn	Al	Other
304H	19	9	Bal.		0.07	0.75			
316H	17	12	Bal.		0.07	0.75	2		Mo2.5
321H	18	10.5	Bal.		0.07	0.75	2		TixC+N
347H	18	10.5	Bal.		0.07	0.75	2		Nb8xC
309H	23	13.5	Bal.		0.07	0.75	2		
310H	25	20.5	Bal.		0.07	0.75	2		
85H	19	15	Bal.		0.20	3.5	0.8	1	
253MA	21	11	Bal.		0.08	1.7	0.6		NO. 17, Ce0.04
330	19	35	Bal.		0.05	1.2	1.5		
800H	20	31	48		0.08	0.3	0.8	0.3	Ti0.3
600	16	76	7		0.04	0.2	0.2		
601	23	61	14		0.04	0.2	0.2		
617	22	52	2	12	0.06	0.5	0.5	1.2	Mo9, Ti0.5
625	22	61	2		0.05		0.2		Mo9, Nb3.6

Table II   Newer heat resistant wrought alloys for refining/petrochemical applications, weight %

Alloy	Cr	Ni	Fe	Co	C	Si	Ti	Al	Other
803	27	34	Bal.		0.08	0.3	0.4	0.4	
HK4M	25	25	Bal.	0.25	0.75	0.4	0.4		B0.004
HPM	25	38	Bal.	0.15	1.7	0.4			Mo2, Zr 0.05, B0.01
HR120	25	37	Bal.	1	0.05	0.6	0.1	0.1	W2, Mo2, Nb7 B0.004 N0.2
HR160	28	37	2	29	0.05	2.7	0.45		
AC66	27	32	41		0.05				Nb0.08, Ce0.6
617LCF	22	52	1.5	12.5	0.08	0.2	0.3	1.2	Mo9
45TM	27	47	23		0.08	2.7			N0.08, Re0.10
602CA	25	63	9.5		0.18		0.15	2	Y0.8, Zr0.07

Table III   Nominal composition and mean stress to rupture in 100,000 hours for those heat resistant cast alloys most commonly used in refining and petrochemical applications

	Nominal Composition				Rupture Stress, psi		
Grade	C	Cr	Ni	Other	1600ºF (871ºC)	1800ºF (982ºC)	2000ºF (1093ºC)
HK40	0.4	25	20		2700	1200	450
HP-45 Nb	0.45	25	35	Nb 1.5	4300	1750	460
HP-45 Nb MA	0.45	25	35	Nb 1.5, Ti, Zr	4700	1850	460
HP-45Nb W	0.45	25	35	Nb 1.5, W 1.5	4400	1850	500
HP-45W	0.45	25	35	W 4	4200	1450	420
HP-45Mo	0.45	25	35	Mo 1.5	3400	1750	500
45Ni-35Cr,MA	0.45	35	45	Nb 1.5, Ti, Zr	4500	1700	600
HP-15Nb	0.15	25	35	Nb 1.5	3500	1500	300

MA=Micro-alloyed

Corrosion Resistance

The importance of this selection criteria is a close second to mechanical properties in terms of optimizing performance. Without adequate corrosion resistance (or corrosion allowance), the component will fall short of the minimum design life desired. In the refining and petrochemical industries, this is typically set at ten years or more. The additional cost usually associated with choosing increased corrosion resistance during the selection process is invariably less than that due to product contamination or lost production and high maintenance costs due to premature failure.

Unlike mechanical properties, there are no codes governing corrosion properties. For some applications or services, recommended practices have been published by the American Petroleum Institute (API), NACE International, etc. Data upon which to base material selection are available in extensive literature and manufacturers' publications. Very reliable data are available from the literature for high temperature corrosion in air and low sulphur flue gases and for some other common refinery and petrochemical environments. However, small variations in the composition of a process stream or in operating conditions can cause very different corrosion rates. Therefore, the most reliable basis for material selection is operating experience from similar plants and environments or from pilot plant evaluations.

Stability Of Properties

The properties of materials used at elevated temperatures may degrade from a variety of causes. The consequences of this degradation depend on the process and the expecta-
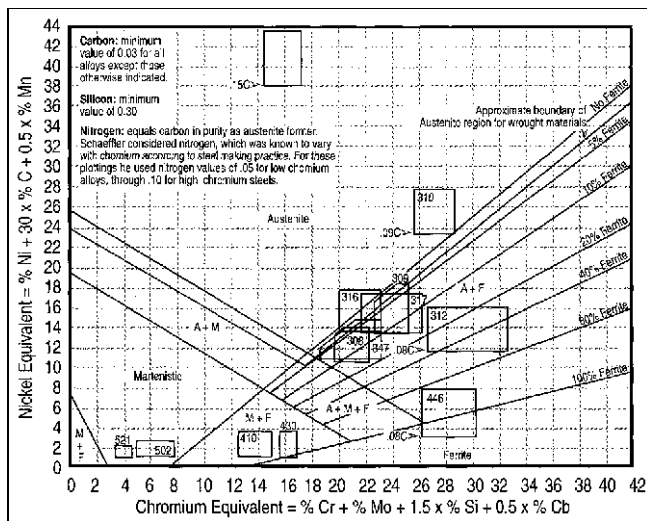

Figure 3 Schaeffler Diagram showing the phases present in various stainless steels as a function of their composition

tions of the material. For example, consider a material in which the intermetallic phase, sigma, can form.

Sigma Phase

In ferritic stainless steels this phase is composed of iron and chromium alone. In austenitic stainless alloys, it is much more complex and will include nickel, manganese, silicon, niobium, etc. in addition to iron and chromium. Sigma phase forms in ferritic and austenitic stainless steels from ferrite, or metastable austenite, during exposure at 1100-1700ºF (593-927ºC). It causes loss of ductility and toughness at temperatures under 250-300ºF (120-150ºC) but has little effect on properties in the temperature range where it forms unless the material has been put into service with considerable residual cold work. In this case, creep strength can be adversely affected. Otherwise, as long as the component continuously operates at the elevated temperature, there will be little consequence. However, care must be taken to avoid impact or suddenly applied high stress when the unit cycles to the lower temperature range. Cracking could occur if the component were impacted or stressed during maintenance work. Formation of the chi-phase during exposure in the above elevated temperature range also causes low temperature embrittlement. Both of these phases can be redissolved by holding the material at 1850-1950ºF (1010-1066ºC) for 1-4 hours depending on thickness and amount of sigma that has formed.

Over time, sigma phase formation is unavoidable in many of the commercial alloys used within the temperature range where it forms. Fortunately, few failures have been directly attributed to it. However, if a component is to be exposed in the critical temperature range and subsequently subjected to extensive cyclic conditions or to shock loadings, an immune or more stable material should be used. Increased resistance or immunity is achieved by selecting a composition that is balanced with respect to austenite vs. ferrite-forming elements so that no free ferrite is present. This can be determined using the Schaeffler diagram *(Figure* 3) or the more recently developed Welding Research Council-92 diagrams. Alloy 800 is not immune but is less susceptible to sigma formation than the 300 series of stainless steel.

Sensitization

Another form of elevated temperature degradation of austenitic stainless steels is sensitization. This is caused by the precipitation of chromium carbides preferentially at grain boundaries *(Figure 4)*. The immediately adjacent chromium-depleted zone is susceptible to accelerated corrosion in some aqueous corrodents. Sensitization can occur during fabrication from the heat of welding, improper heat treatment or through service exposure in the temperature range of 900-1500ºF (480-815ºC). Sensitization has little or no effect on mechanical properties but

can lead to severe intergranular corrosion in aggressive aqueous environments such as polythionic acid. Polythionic acid can form during downtime on equipment that has been even mildly corroded by hydrogen sulphide at elevated temperature. The iron sulphide corrosion product combines with air and moisture to form the acid and induces intergranular corrosion and cracking.

To minimize the chance of sensitization during fabrication, carbide forming stabilizers are added to certain stainless steels. The most common are titanium (Type 321) and niobium (Type 347). As long as their lower strengths are taken into account, another alternative is to use low carbon grades (Types 304L, 316L) with carbon <0.03%. To minimize the effects of frequent or continuous exposure within the susceptible temperature range, a thermal stabilization treatment of Type 347 at 1600-1650ºF (870-900ºC) for 4 hours is recommended. Type 321 does not respond acceptably to this treatment. Use of the low carbon grades would be better still on the basis of stability. However, their lower strength and/or code limitations may preclude this alternative.

The higher carbon content of heat resistant alloys and the presence of other elements cause these alloys to "age" during exposure to elevated temperatures. Aging results from formation of secondary carbides and other precipitates. This usually results in higher strength but also causes loss of ductility at ambient temperature leading to potential fabrication problems. This is more of a problem with cast than wrought heat resistant alloys because of the typically higher original carbon content.

Recovery from all of the above forms of degradation is possible by solution annealing the material at temperatures appropriate for the alloy grade followed by rapid cooling. For the 300 series stainless steels, annealing can be done at 1950ºF (1066ºC) while the high carbon heat resistant alloys may require treatment as high as 2150ºF (1177ºC). Recovery is not permanent. Re-exposure to the causative conditions will result in re-degradation.
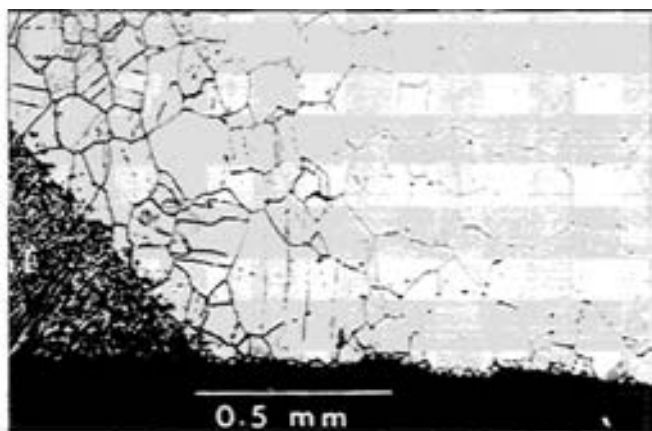

Figure 4 An example of grain boundary sensitization in a Type 304 stainless steel exposed to operating temperatures of 1250-1350ºF (677-732ºC)

Fabricability

There are many outstanding materials with highly desirable mechanical properties and corrosion resistance which are seldom used because they cannot be fabricated. There are few refinery or petrochemical plant applications where welding or bending or some other forming operation is not required to construct a useable piece of equipment. Also, there are some materials which have excellent properties that can be fabricated as produced but, because of "aging", cannot be modified or repaired after exposure to operating conditions. Therefore, materials must be selected based on their maintainability as well as their original fabricability. In general, the wrought heat resistant alloys have greater fabricability than the cast materials. This is in part due to the dendritic structure of the latter and to the addition of alloying elements in concentrations that cannot be tolerated by the wrought materials during the severe production operations to which they are subjected (rolling, forging, etc.). The cast alloys typically can tolerate significantly higher concentrations of carbon, silicon, tungsten, molybdenum, etc. which are added to enhance mechanical properties, corrosion resistance, or both. But, these elements also can adversely affect the original, as-produced fabricability and make maintainability, particularly weldability, difficult, if not impossible.

Availability

Materials engineers and purchasing agents become frustrated in trying to obtain materials that have a limited number of producers or a limited production volume. Such frustration can be particularly high when a small amount of material is needed to finish a job or replace a failed piece. Prior to the original specification of a material, consideration should be given to its future availability for repairs or replacement in the form or forms that it will be used. In those cases where it might not be available, alternative replacement materials should be identified. This will be extremely helpful 5 or 10 years later when the optimum original material may not be available to the maintenance engineer.

Cost

Economics enter into every business decision. But, the important criteria should not be the initial cost of a material. Its life-cycle cost or cost effectiveness should govern instead. It usually is much more cost effective to specify a material that will provide an extended life, particularly in areas that are difficult to repair or in components that would cause major shut-downs in case of failure. In these situations, the original cost of the material can be insignificant compared to the loss of production caused by the use of a lower cost, but less effective, material. Unfortunately, com-

petitive bidding and corporate bottom lines frequently create barriers that inhibit realization of long equipment life. The enlightened company will recognize the value of the life-cycle cost approach on long-term financial health and not embrace only the low initial cost option.

Principal Forms Of High Temperature Corrosion

Although some examples of application at lower temperatures are discussed, as stated earlier, the focus of this publication is on alloy applications at temperatures above 1200°F (650°C). *Table* IV lists the most common forms of corrosion encountered in this temperature range. Often, more than one of these forms are acting to degrade the metal. For example, a furnace tube could be corroding on the outside from the oxidation mechanism while simultaneously being carburized on the inside. This possibility makes the materials engineer's choice even more complex.

Table IV   Principle forms of high temperature corrosion

- Oxidation;
- Sulphidation;
- Carburization;
- Metal dusting;
- Nitridation;
- Halogen corrosion;
- Fuel ash corrosion.

Oxidation

This is the most commonly encountered form of high temperature corrosion. However, oxidation is not always detrimental. In fact, most corrosion and heat resistant alloys rely on the formation of an oxide film to provide corrosion resistance. Chromium oxide is the most common of such films. As temperature is increased, the rate of oxidation also increases and becomes deleterious. Increased chromium content is the most common way of improving oxidation resistance. The effect of chromium on the rate of oxidation of several alloys in air is shown in *Figure5*.(1) The rate of oxidation for these same alloys would be somewhat lower in a typical low sulphur flue gas. (2)

Other elements including aluminum, silicon and some of the rare earths are often added to enhance oxidation resistance. Because of resulting instabilities, fabrication difficulties or for other reasons, there are limits to the amount of these elements that can be added. Few alloys contain more than 30% chromium. Silicon is usually limited to no more than 2% and aluminum to less than 4% in wrought alloys. Yttrium, cerium and the other rare earths are usually added only as a fraction of a percent.

Increasing the nickel content of the austenitic stainless steels up to about 30%, with relatively constant chromium content, dramatically reinforces the effect of chromium on oxidation resistance as shown in *Figure 6*.(3) Some continued improvement occurs at higher concentrations but at a much diminished rate. Higher nickel content causes the oxide to be more resistant to spalling and in
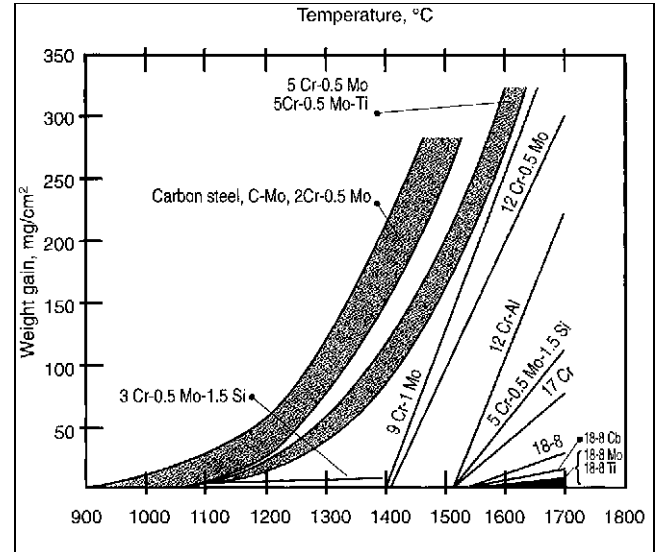

Figure 5   Oxidation resistance of steels in air after 1000 hours at temperatures of1100-1700°F (590-930°C). Ref. 1
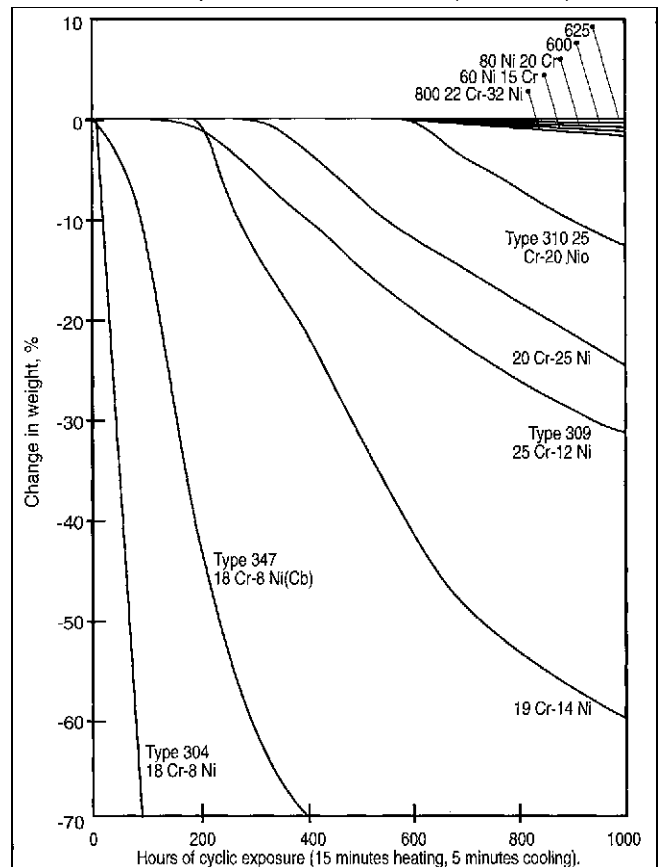

Figure 6   Cyclic oxidation resistance of stainless steels and nickel-base alloys in air at 1800°F(980°C). Ref. 3

creases the metallurgical stability of the composition.

High temperature oxidation rates can vary significantly for quite similar centrifugally cast, modified HP heat resistant alloys as shown in *Figure* 7. These alloys are commonly used in ethylene cracking and reformer furnaces. The comparative oxidation rates shown were extrapolated from cyclic tests conducted in air over a period of 500 hours at 1960°F (1070°C) and 2100°F (1150°C). The rates shown are unlikely to be sustained in longer, continuous exposures but do demonstrate that differences
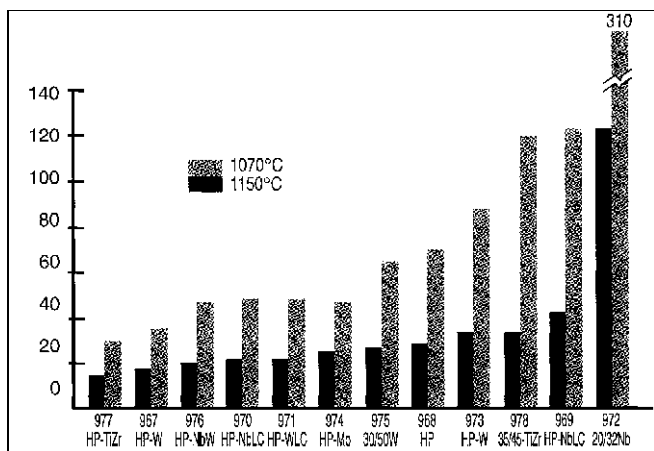

Figure 7 Annual oxidation rates for centrifugally cast heat resistant alloys. Rates are extrapolated from 500 hour cyclic exposure in air
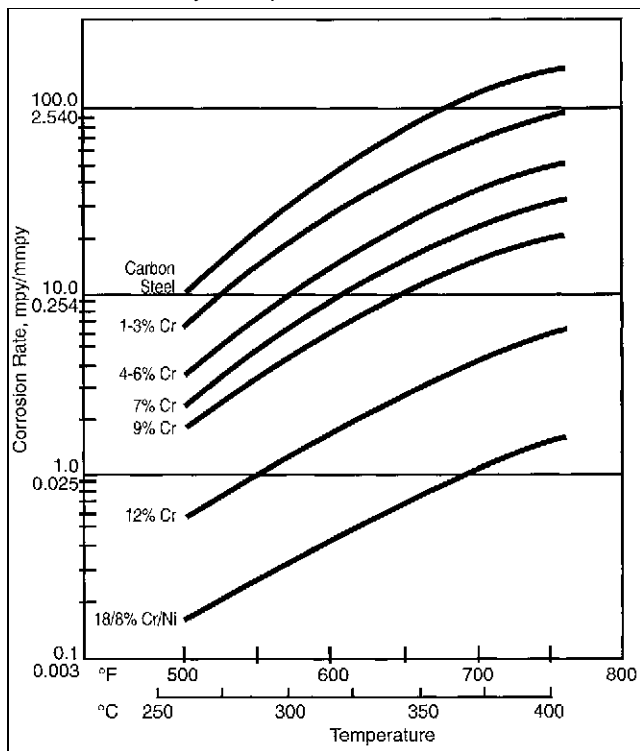
in performance can be expected between alloys of similar composition produced by different suppliers. This difference is most notable at the higher temperature. Of particular note are the paired Alloys 967/973 and 969/ 970 at 2100°F (1150°C). Alloy 972, 25Cr-32Ni, was included for comparison with the higher alloys. Excessive oxidation rates are rarely a cause of reformer or ethylene furnace tube failures but can be indicative of coking and carburization tendencies.

Sulphidation

Organic sulphur compounds such as mercaptans, polysulphides, and thiophenes, as well as elemental sulphur, contaminate practically all crude oils in various concentrations. These contaminants can cause heavy corrosion at lower temperatures but are especially aggressive in refining operations above 500-550°F (260-288°C). This is a result of their partial conversion to corrosive hydrogen sulphide during atmospheric distillation. Usually this form of sulphur corrosion can be handled adequately with the 5 to 9% Cr-Mo alloys unless the crude also contains naphthenic acids. In that case, Type 316 or Type 317 stainless steel is required. Sulphur corrosion rates are shown in *Figure 8.*

Elemental sulphur and any remaining unconverted sulphur compounds are converted to hydrogen sulphide through hydrogenation processes and subsequently removed by amine or similar recycle treatment processes. Hydrogen sulphide in the presence of hydrogen becomes extremely corrosive above 500-550°F (260-288°C) and the austenitic grades must be used to avoid excessive scaling or potential catastrophic sulphidation. Excessive scaling not only shortens equipment life but also adversely affects operations by fouling downstream catalyst beds and exchanger bundles. Hydrogen - hydrogen sulphide corrosion
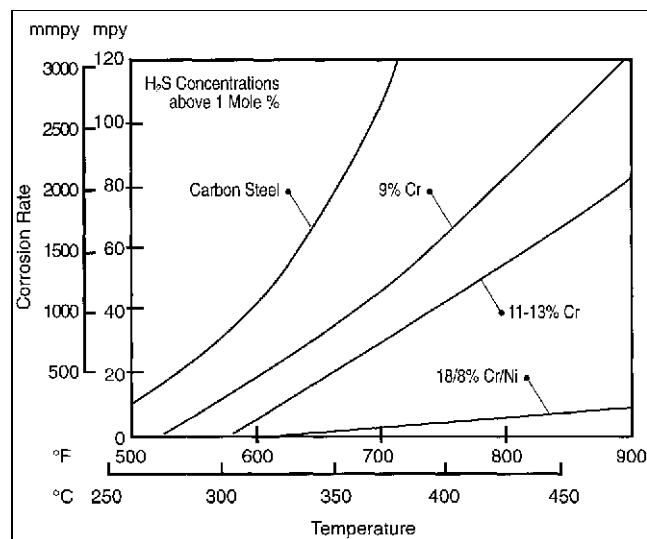

Figure 8 Corrosion rates for carbon steel, Cr-Mo alloys and stainless steels in a hydrogen-free, hydrogen sulphide environment

Figure 9 Shows significantly higher corrosion rates for some of the same materials in *Figure 8* when hydrogen is present in a H2/H2S environment.

rates are shown in *Figure 9.*

Any of the 18 Cr-8Ni, stainless steel grades can be used to control sulphidation . However, it is best to use the stabilized grades mentioned earlier. Some sensitization is unavoidable if exposure in the sensitizing temperature range is continuous or long term. Stainless equipment subjected to such exposure and to sulphidation corrosion should be treated with a 2% soda ash solution or an ammonia solution immediately upon shutdown to avoid the formation of polythionic acid which can cause severe intergranular corrosion and stress cracking.

Vessels for high pressure hydrotreating and other heavy crude fraction upgrading processes (eg. hydrocracking) are usually constructed of one of the Cr-Mo alloys. To control sulphidation, they are internally clad with one of the 300 series stainlesses by roll or explosion bonding or by weld overlay. In contrast, piping, exchangers, valves, etc. exposed to high temperature hydrogen-hydrogen sulphide environments are usually constructed of solid 300 series stainless alloys. In some designs Alloy 800H has been used for piping and headers. In others, centrifugally cast HF-modified piping has been used.

High nickel alloys are rarely used in refinery or petrochemical plants in hydrogen-hydrogen sulphide environments because of their susceptibility to the formation of deleterious nickel sulphide. They are particularly susceptible to this problem in reducing environments. Although high chromium helps, as a general rule, the higher the nickel the more susceptible the material.

Vapour diffusion aluminum coatings (Alonizing™) have been used with carbon, Cr-Mo and stainless steels to help control sulphidation and reduce scaling. For the most part, this has been restricted to smaller components. Aluminum metal spray coatings have also been used but not widely nor very successfully.

Multiple Environments

A dilemma occurs in designing equipment that requires resistance for variable times of exposure to multiple environments such as oxidizing and sulphidizing conditions. If the predominant amount of time involves exposure to oxidation - with minimal but occasional exposure to sulphidation - it may be prudent to design with a high-nickel, high-chromium alloy, such as some of the newer-alloys listed in *Table II* (HR-120, HR-160, Alloy 602CA or Alloy 45TM). If the environment is purely sulphidizing, a low-nickel, high-iron, high-chromium alloy would be the best choice. Sulphidation resistance for highly reducing conditions can be enhanced by high aluminum or silicon contents and by keeping the chromium above 15% with a low Ni/Fe ratio.

Carburization

Carburization can occur when metals are exposed to carbon monoxide, methane, ethane or other hydrocarbons at elevated temperatures. Carbon from the environment combines primarily with chromium but also with any other carbide formers (Nb, W Mo, Ti, etc.) present in the alloy. As a result, the carbides may be quite complex. They form within the grains and along grain boundaries. The carbides are strong and hard but very brittle. The overall effect is to drastically reduce ductility at temperatures up to 900-1000ºF (482-538ºC). By tying up the chromium, carburization also reduces oxidation resistance. It also adversely affects creep strength and because of the volume increase associated with the carbon uptake and carbide formation, it imposes additional stress that contributes to mechanical failure. These stresses are evidenced often by the localized bulging of tubes that are locally carburized. An example of carburization is shown in *Figure 10.*

Carburization is not a common occurrence in most refining operations because of the relatively low tube temperatures of most refinery fired heaters. However, it
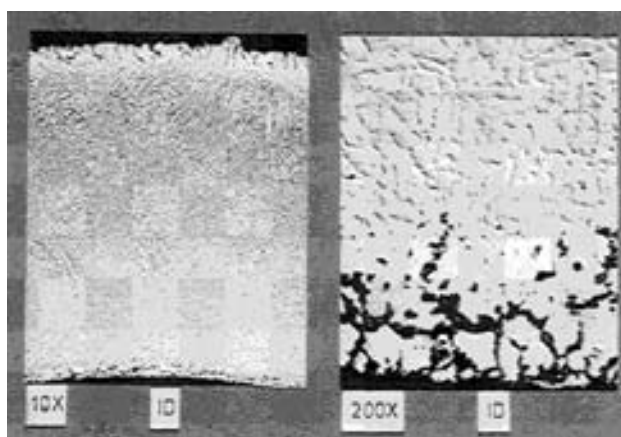

Figure 10 A typical example of a heavily carburized HP-Nb type tube with oxidation occurring at the chromium-depleted ID
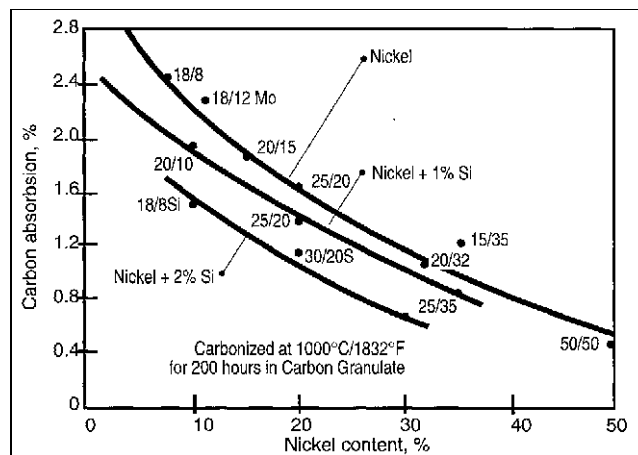

Figure 11 Effect of nickel on the resistance of Cr-Ni alloys to carburization. Ref. 4

can and does occur in those higher temperature process heaters (eg. cokers) where its control in 9Cr-Mo tubes has been somewhat successful through the use of an aluminum vapour diffusion coating (Alonizing™). Carburization can also occur during an upset which results in the exposed material being heated to unacceptably high temperature. Where it is expected to occur within the range of normal operating conditions, the broader approach has been to use Type 304H for temperatures up to about 1500ºF (816ºC). There is no advantage in using either of the stabilized grades since any unreacted titanium or niobium from the original melt would be quickly tied up. Type 310 or Alloy 800H may be used for temperatures up to about 1850ºF (1010ºC). For the most part, refinery application of the latter two alloys for this purpose is confined to hydrogen reformer furnaces. Unfortunately, the 300 series stainless alloys, including Type 310, are subject to sigma phase embrittlement in the temperature range where they have useful carburization resistance. Alloy 800H would be a better choice.

The most effective element in controlling carburization is nickel in combination with chromium. As shown in *Figure 11* (4), absorbed carbon is plotted against nickel content with carbon absorption shown to decrease with increased nickel content. Silicon is also shown to have a strong effect. Aluminum in excess of 3.5-4% also is beneficial. Unfortunately, the presence of much more than 2% Si adversely affects the rupture strength and weldability of both wrought and cast heat resistant alloys. Aluminum, in concentrations higher than 2-2.5%, has an adverse effect on ductility and fabricability – properties that are essential for piping, tubing, pressure vessels, etc.

Coatings and surface enrichment using silicon, aluminum, chromium, and combinations thereof, have been tried to control carburization of heat resistant alloys. Unfortunately, none of these have been successful for the long term. Vapour diffused aluminum enrichment showed promise and performed well at lower temperatures but broke down after relatively short times at temperatures above 1850-1900ºF (1010-1040ºC).

Carburization is far more common in the petrochemical industry than in refining. The most common occurrence is in the radiant and shield sections of ethylene cracking furnaces. Carburization is a serious problem in these furnaces because of the high tube metal temperatures – up to 2100ºF (1149ºC) – and high carbon potential associated with the ethane, propane, naphtha and other hydrocarbon feedstocks which are cracked. However, it also occurs, albeit less frequently and with less severity, in reforming operations and in other processes handling hydrocarbon streams or certain ratios of $CO/CO_2/H_2$ gas mixtures at high temperatures.

A survey(5) published in 1981 indicated that carburization was the most frequent cause of ethylene furnace tube replacement. Most furnaces of that era were tubed with centrifugally cast HK-40, wrought Type 310 or Alloy 800/800H. Since the mid-1980s, more resistant, centrifugally cast, modified HP alloys *(Table III)* have been more commonly used but carburization appears to continue to be the primary cause of tube replacement. This is probably due to more severe operating conditions – mainly higher temperatures. Some operators are beginning to use the higher 35Cr-45Ni cast alloy, with various additions, to combat these conditions. For short residence time furnaces, tubed with small (<1.5 in. ID) tubes which cannot be cast, wrought alloys including HK4M and HPM, Alloy 803 and Alloy 800H *(Tables I, II)* are being used. Although these alloys do not appear to have carburization resistance equivalent to the modified-HP or higher Cr-Ni alloys, longer term, in-service experience is required upon which to base comparisons. Other wrought alloys (eg. 85H and HR-160, both with high silicon) are used successfully to combat carburization of trays, retorts and other components used in carburizing treatments. However, their limited fabricability precludes broad use in the refining or petrochemical industry.

The rate of carburization of ethylene cracking tubes of a given alloy is process driven. As mentioned earlier, temperature and carbon potential are the primary factors affecting its rate. Increasing steam dilution will reduce the rate. The type of feed is also a factor with lighter feeds generally being more aggressive than heavier feeds because of their higher carbon potential. Some operators pre-sulphide their coils while others use feedstock with crackable sulphur present or added. Ostensibly, this reduces the catalytic characteristics of the tube surface and reduces coke formation. This, in turn, reduces the frequency of decoking which many believe to be a major cause of carburization.

The form and severity of decoking operations appear to play important roles in the rate of carburization. High temperature decoking with low quantities of steam are thought to accelerate carburization. Likewise, steam/ air decoking appears to be more deleterious than steam only. (6) Appropriate metallurgy can be used to reduce but rarely totally eliminate carburization. The most important characteristic of a successful alloy is its ability to form and maintain a stable, protective oxide film. Chromium oxide is considered to be such a film. However, it is not sufficiently stable at the higher operating temperatures and low oxygen partial pressures. Alumina or silica are much better. Unfortunately, the addition of aluminum or silicon to the heat resistant alloys in quantities to develop full protection involves tradeoffs in strength, aged ductility, and/or weldability that are often unacceptable. Viable alloys are generally restricted to about 2% of either element. This

is helpful but not a total solution.

Carburization is Very Non-uniform

One insidious aspect of carburization of ethylene furnace tubes and some other equipment is its unpredictability and its non-uniform nature. Models have been developed, based on operating experience, that can be used with some modicum of success to predict the general rate of carburization. Unfortunately, none of the known models are completely accurate or acceptable. The primary reason is the non-uniform manner in which carburization occurs. This non-uniformity is demonstrated in *Figures 12* and *13* which show eleven representative tube sections removed from a furnace after several years operation under identical conditions. The transverse sections were removed from the same location in each tube and from the same end of the longitudinal sections shown in *Figure 13*.

These examples show that not only can the degree of carburization vary dramatically around the circumference of tubes but also over very short distances along the length of the tube. Thus, temperature alone is not a determining factor. Surface condition was identified as a major factor many years ago but again, is not a singularly effective factor since these tubes were initially identical and saw the same service conditions for many years. This non-uniformity also presents a problem in interpreting the results of measurements of the degree of carburization.

Carburization causes the normally non-magnetic wrought and cast heat resistant alloys to become magnetic. The resulting magnetic permeability has been used for many years to assess the degree of carburization that has occurred. Measuring equipment used ranges from the hand held magnet to the more technologically sophisticated, multi-frequency eddy current instruments in use today. While the latter can be helpful in determining not only the degree of carburization but its pattern as well, care must be exercised in interpreting the results because of the variability discussed earlier. There
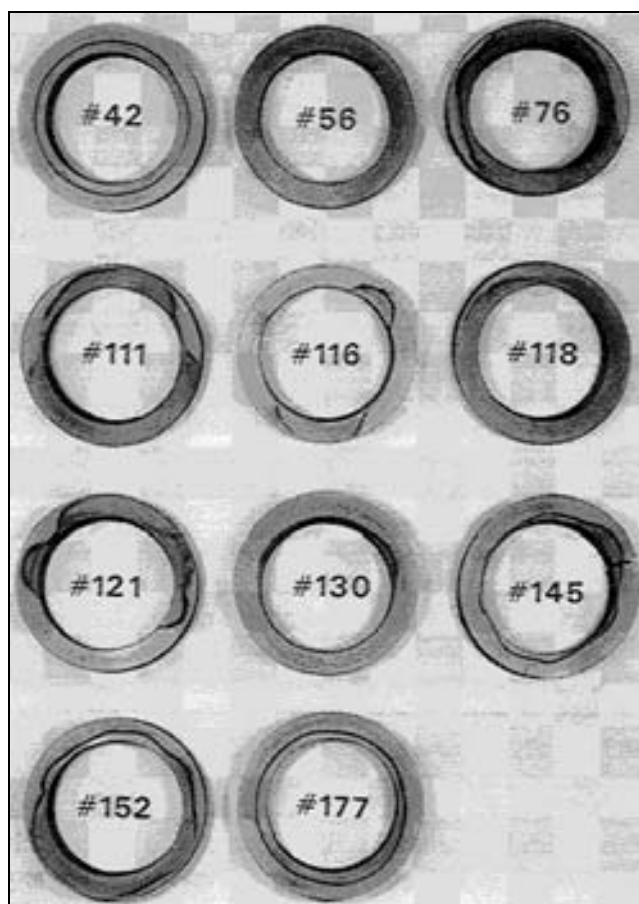
Figure 12 Transverse sections of HP-Mo type tube sections removed from identical positions in an ethylene cracking furnace after several years service. Note the varying degrees of carburization from tube to tube and around the circumference
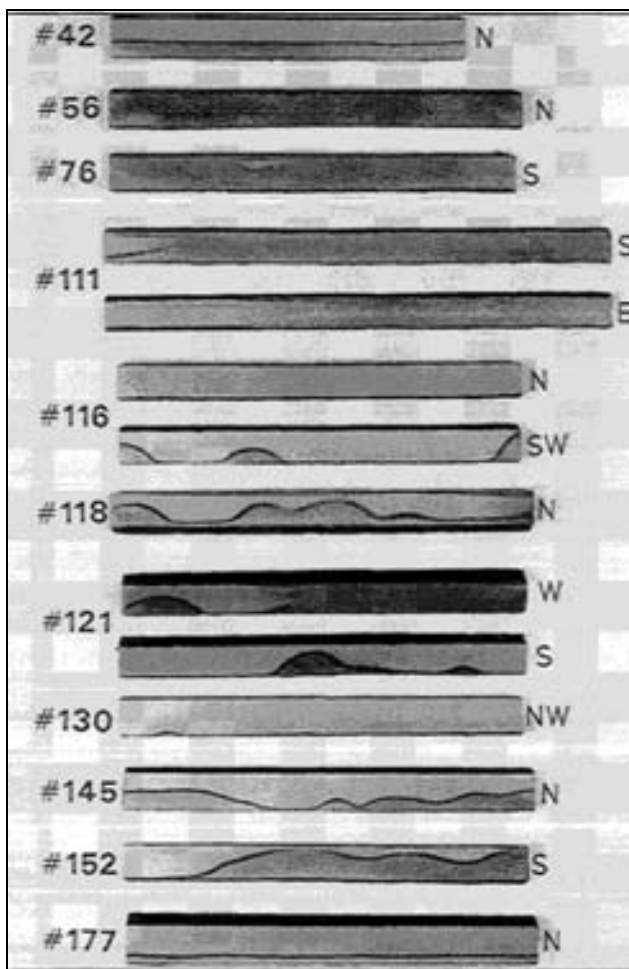
Figure 13 Longitudinal sections of the same tubes as in *Figure 12* show great variation in the degree of carburization within very short distances and from tube to tube

are other benefits from such surveys of radiant section coils. Carburization patterns can reveal uneven firing patterns that might otherwise have gone undetected. They can also be helpful in implementing selective metallurgical alternatives for tube alloys. In multi-tube coils, for example, the upstream tubes could be made of the lower cost, lower nickel modified HP alloys and outlet tubes of the higher cost, but more resistant, 35Cr-45Ni alloys.

Metal Dusting

Metal dusting is considered to be a form of carburization experienced in some refining and petrochemical processes. While some of its characteristics are similar, it differs in many ways from classical carburization. It can cause extremely rapid loss of metal which normal carburization does not and the depth of carburization in advance of the metal loss is usually quite shallow, but intense. Most often it is associated with CO-rich $CO/CO_2/H_2$ gas streams often associated with reforming, synthesis gas, partial oxidation or other processes.

It typically occurs in the temperature range 900-1600ºF (482-871ºC) with peak reaction rate at 1300-1350ºF (704-732ºC). The reaction rate can be very rapid and the results catastrophic. It causes damage usually taking the form of rounded pits with a dusty surface. It is rather unpredictable and most of the stainless and heat resistant alloys can be attacked. Gas diffusion aluminum coatings have been used effectively and, when they can be added, steam, sulphur or ammonia also can be used for its control. The most positive cure, however, is to adjust the gas composition by reducing the CO partial pressure.

Nitridation

Similar to carburization, nitridation occurs when chromium and other elements combine with nitrogen to form embrittling nitrides. Nitridation usually occurs when carbon, low alloy and stainless steels are exposed to an ammonia-bearing environment at elevated temperatures. As in the case of carburization, higher nickel alloys are very resistant to nitridation attack due to the low solubility of nitrogen in nickel. Alloy 600, with 72% nickel, is often used in the heat treating industry and occasionally in refining and petrochemical applications involving ammonia at temperatures above 650ºF (343ºC). Economics and lower strength, compared with Alloy 800H and cast modified HP, have minimized its applications in the refinery and petrochemical industries. These alloys are not immune to attack but are more cost effective.

Although the nitrogen molecule is quite stable, sufficient dissociation does occur at combustion temperatures to cause nitridation of 800H or HP-type furnace tubes at metal temperatures of 1850ºF (1010ºC) and higher.

Halogen Corrosion

Halogens, especially dissociated chlorine (chloride ions), frequently contaminate refinery and petrochemical feed streams and can lead to serious corrosion problems. Most common of these is chloride stress corrosion cracking of the austenitic stainless steels that can occur at temperatures above 120ºF (50ºC) in aqueous solutions containing quite low concentrations of chloride. The halogen salts are also very corrosive. Ferric chloride, for example, is added to acid solutions as a standard test to evaluate the pitting resistance of alloys. Chlorides and fluorides contribute to high temperature corrosion as well by interfering with the formation of protective oxides or breaking them down if already formed.

In refining operations, chlorides most commonly enter the process operations as salt water or brine. Most of this material is removed in desalters. The residual is hydrolysed during atmospheric distillation and is absorbed in the overhead condensate. If not neutralized, this condensate can be very corrosive. Occasionally, organic chlorides find their way into crude feed. These are not removed in the desalters but are generally removed in the distillation process. Chlorides can get into the downstream processes from slop rerun, cooling water leaks (from a salt water system) or from salt water contamination during shipment of semi-finished product. Fluoride contamination is usually the result of blending streams from an alkylation operation.

This downstream contamination not only can affect refining equipment but also impact on petrochemical facilities which take feed from these sources. Petrochemical facilities are more subject to feed contamination during shipment or storage. The latter is often done in salt domes which can be a source of chlorides.

The high temperature halogen attack mechanism is similar to that for oxidation and sulphidation except scales do not generally form because of the volatility of the corrosion products.(7) Resistance to high temperature halide attack increases with increasing levels of both nickel and chromium. The high nickel alloys are significantly more resistant than the stainless steels to chlorine but not fluorine which is more soluble in nickel. The stainless steels are more resistant than the lower alloyed steels. Minimizing Mo and W helps the resistance of alloys to oxidizing halogen corrosion, while aluminum improves the resistance of nickel-base alloys. (8)

Fuel Ash Deposits

Some refinery heaters, boilers, etc. are fired with "dirty" fuels. This requires the use of special alloys that are not only heat and oxidation resistant but can also resist corrosion by fuel ash deposits containing vanadium, sodium and/or sulphur present in the fuel used. The melting point of one of these mixed compound deposits

(Na$_2$SO$_4$-V205) can be as low as 1166ºF (630ºC) at which point corrosion can be catastrophic. The 50Ni-50Cr-Nb alloy is about the only alloy that can be used for hangers, tubesheets, supports, etc. when their operating temperatures approach or exceed this temperature. "Dirty" fuels are not used in reformers or ethylene furnaces because of the catastrophic corrosion that would occur at their high operating temperatures. And, use of the 50Ni-50Cr alloy for all of the high temperature components would neither be practical nor cost effective for the latter applications.

Refinery/Petrochemical Applications Of Wrought And Cast Heat Resistant Alloys

As stated earlier, the Ni-Cr-Fe alloys are extensively used in refining and petrochemical plant equipment for both liquid and gaseous low temperature corrosion resistance and for heat resistant applications. In refining operations, most equipment that operates below 500-600ºF (260-316ºC) is constructed of carbon steel or Cr-Mo-Fe alloys. An exception are the alkylation processes where highly alloyed materials are required to handle streams containing some sulphuric or hydrofluoric acid. Other examples would be the use of Types 316 and 317 for handling crude fractions with a high naphthenic acid content and other higher alloys for flue gas desulphurization processes. Since petrochemical plant environments generally are more diverse and often more corrosive, there is more extensive use of the Ni-Cr-Fe and nickel-based alloys in this temperature range.

At temperatures from 600-1000ºF (316-538ºC), there is increased use of the Ni-Cr-Fe alloys in both industries. But the increased usage in refining is probably proportionately greater because of the need for resistance to high temperature sulphidation. Much of the equipment used in hydrodesulphurisation or in the upgrading of heavier fractions must be made of solid or clad 300 series stainless steels. It is for equipment in services above 1200ºF (650ºC) where the stainless and heat resistant alloys are used most extensively in both the refining and petrochemical industries.

The single most important use of both wrought and cast heat resistant Ni-Cr-Fe alloys in refining and petrochemical applications is in fired heaters, such as are shown in *Figure 14*, where they are used for tubes, hangers, supports, tubesheets, etc. Examples of these components can be seen in *Figures 15-17*. Most fired heaters for refining processes operate at tube metal temperatures under 1200ºF (650ºC). Consequently, they can be constructed of carbon or low alloy steels. However, for aggressive environments which can cause sulphidation, carburization or other forms of corrosion, even at lower temperature, the stainless or heat resistant grades must be used as discussed earlier. Coker heaters and those in desulphurization service are two examples that would require the higher alloys – at least in the radiant section.

At temperatures above 1200ºF (650ºC), the higher carbon content stainlesses (Types 304H, 316H, 321H, 347H, 309H) or more highly alloyed heat resistant grades (ie. Type 310, Alloy 800H) must be used for their oxidation resistance and strength. Above 1500ºF (816ºC), the Ni-Cr-Fe and nickel-based alloys are required. With the exception of catalytic steam hydroformers for hydrogen production, there are no fired heaters in the refining industry that operate above 1500ºF (816ºC).

Fluid Catalytic Cracking Units (FCCU)

Other than steam reforming, this is the only other common refining process that has some critical components operating at temperatures in excess of 1200ºF (649ºC). Regenerator cyclones are made of Types 304/304H and 321/321H while Type 304H is used for the high temperature small diameter piping around both the regenerator and
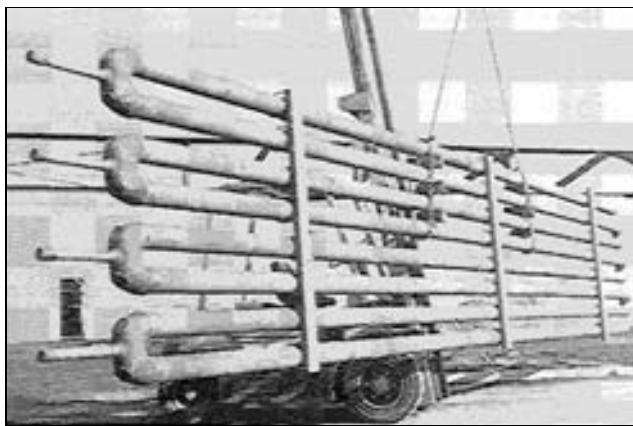

Figure 14 Fired heaters typical of those found in the refining and petrochemical industries

Figure 15 Assembled coil of centrifugally cast tubes joined by statically cast return bends -both in HP-Nb alloy. For use in a "conventional" ethylene cracking furnace. Photo courtesy of Paralloy Ltd.

reactor. The cast versions of these alloys have been used for high temperature FCCU valves but these are generally below 1200ºF (649ºC). Expansion bellows in the regenerator catalyst standpipe have been problem areas, and Alloy 800 has been used with some success in this application. (9) Alloy 617LCF, a recently introduced modification of the popular aerospace alloy, has been suggested for this application because of its superior low cycle fatigue and creep properties.

Catalytic Steam Reformers for Hydrogen/Ammonia/Methanol Production

Catalytic steam reforming is a widely used process for the production of hydrogen for use in refinery hydrogenation processes and for the production of ammonia and methanol in the petrochemical industry. Much use is made of heat resistant alloys in the primary reformer furnace which is a key component in this process. They are also widely used for the other components from the primary reformer through the waste heat boiler. These components typically operate at temperatures of 1300-1850ºF (704-1010ºC) and at high pressures. In most designs, vessels and large piping are refractory-lined to conserve heat and to take advantage of higher metal strength at lower temperatures. To prevent erosion, these linings are frequently shrouded with relatively thin sheets of Type 304 – up to 1500ºF (816ºC) – and Type 310 or Alloy 800 at higher temperatures.

Materials for unlined components are required to have good high temperature strength, good ductility and good thermal fatigue properties. Alloy 800H has been used successfully for catalyst tubes, pigtails, header manifolds, high temperature transfer piping between the primary and secondary reformers and for secondary reformer internal parts. However, cast catalyst tubes are more commonly used than Alloy 800 in reformer furnaces. These have been most frequently made of centrifugally cast HK-40, HP-Nb or IN-519. Tubesheets, fittings and other components are made of these alloys in the form of static castings. In general, HK-40 is being phased out in favour of HP-Nb because of the latter's higher strength and better oxidation resistance. With its higher strength, the tube wall of HP-Nb can be thinner thereby increasing the catalyst capacity of the same size tube. More important, thermal stress is reduced thereby helping to improve tube life. And, thermal effi-
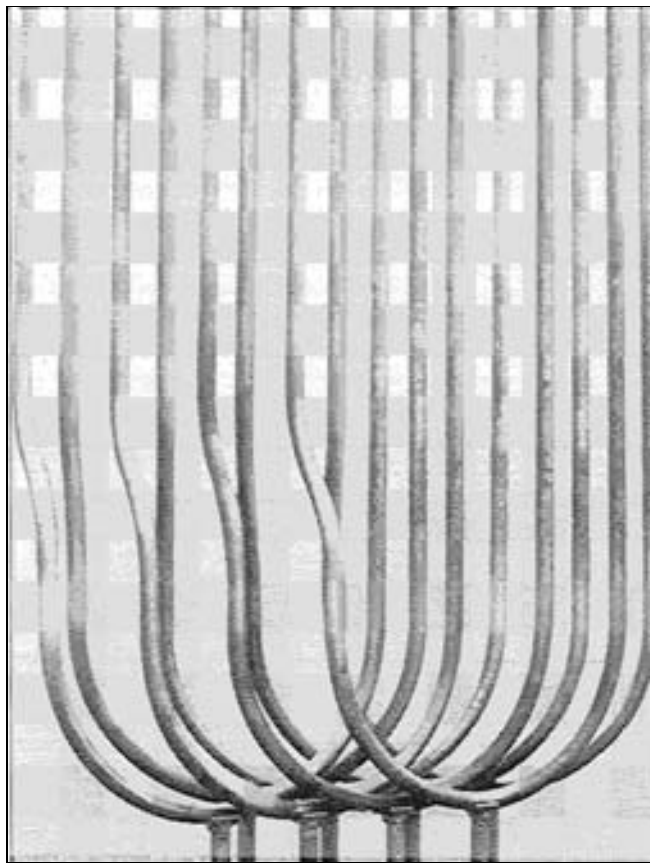

Figure 16 Assembled coils of small diameter tubes centrifugally cast in HP-Nb for a short residence time ethylene cracking furnace. The bent sections are usually made from a lower carbon version of the same alloy. Photo courtesy of Paralloy, Ltd.
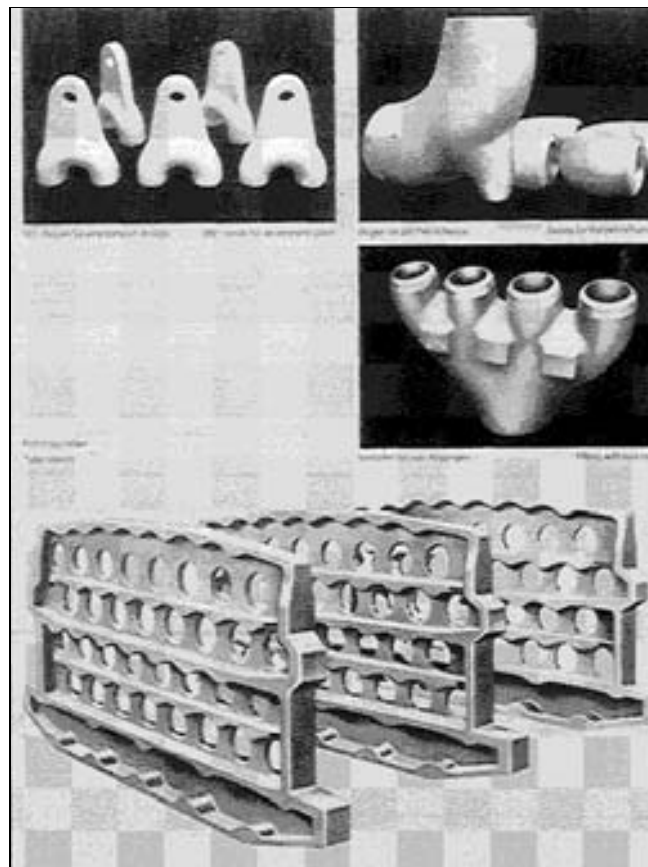

Figure 17 Statically cast tube sheets (bottom) and fittings (inserts) of HP-Nb alloy.
Photo courtesy of Pose-Marre, Gmbh.

ciency is improved. Ammonia reformer furnaces are said to be the largest single application for the HP-Nb alloy. (10)

Centrifugally cast 20Cr-32Ni-Nb alloy is a common alternative to 800H for outlet header manifolds. Some of the secondary reformer internals may be exposed to temperatures as high as 2100°F (1149°C). Strength is less of a factor for these components than oxidation, carburization and nitridation resistance. The waste heat boiler typically takes 1800°F (982°C) effluent from the secondary reformer to generate steam at up to l500psi(10.3Mpa).(11) Alloy 600 is frequently used for cladding tubesheets and for ferrules on the hot inlet end where the tubesheet is typically protected by a refractory layer. Throughout the process, Type 304H is used for components at the lower end of the process temperature range.

Ethylene Cracking

In ethylene production, the hydrocarbon feeds (ethane, propane, naphtha, gas oils, etc.) are thermally cracked in the presence of steam at low pressure and process temperatures of 1450-1550°F (788-843°C). The radiant section of some of these cracking furnaces operate at end-of-run tube metal temperatures up to 2100°F (1149°C). This is the practical upper limit for most of the fabricable, heat resistant alloys.

The shield section, the lower convection section, the outlet transfer line and the quench unit of the ethylene cracking furnace operate at significantly lower temperatures but also must be made of heat resistant alloys. For the tubes and other components, Alloys 800 and 253MA have been used successfully up to 1850-1900°F (1010-1038°C). However, radiant and shield tubes more often use the centrifugally cast modified HP family of alloys – even at the lower temperatures. The most commonly used of the alloys of this family is the HP grade with niobium. Others that are used are alloyed with other carbide forming ele-

ments and solid solution strengtheners such as Mo and W. There are also grades, referred to as "microalloyed", which have small amounts of Ti, Zr, and rare earth elements added. The volume of this family of alloys in this application is about two-thirds that for reformers. Recently, some operators have begun to use the higher nickel-chromium (35Cr-45Ni) alloys for their higher temperature operations.

Many of the modified HP alloys are considered proprietary by their developers. However, they are commonly copied with only minor variations. An example is the recent proliferation of the "micro-alloy" grade which was actively marketed by only one supplier in 1986-87. Most major suppliers now offer a similar product. The microalloy additions enhance the stress-rupture properties, as shown in *Figure 18*,(12) presumably through the development of finer, more dispersed carbides. The rare earth addition also appears to improve oxidation and carburization resistance. The effectiveness of micro-alloying is very dependent on the melting and pouring practice. Total deoxidation of the melt and good mixing are required for consistent and improved performance.

The majority of the cast alloys have a carbon content of 0.4-0.5% but there have been low carbon (0.10-0.18%) variants produced for use as sweep bends in some of the short residence time furnaces that use small diameter tubes (~1.5 - 2.5 in. (38-65mm) ID) to improve ethylene yield. Other short residence time furnaces use even smaller diameter tubes that cannot be cast so must be made of Alloy 800H, Alloy 803, HK4M, HPM or another wrought alloy. Two other candidate wrought alloys include AC66 and HR-120.

Wrought tubes can be made in single lengths greater than 40 feet(12m) while the smallest cast tube is restricted to about 9 feet(2.8m). Thus, significant fabricating costs and sources of potential defects are eliminated by using
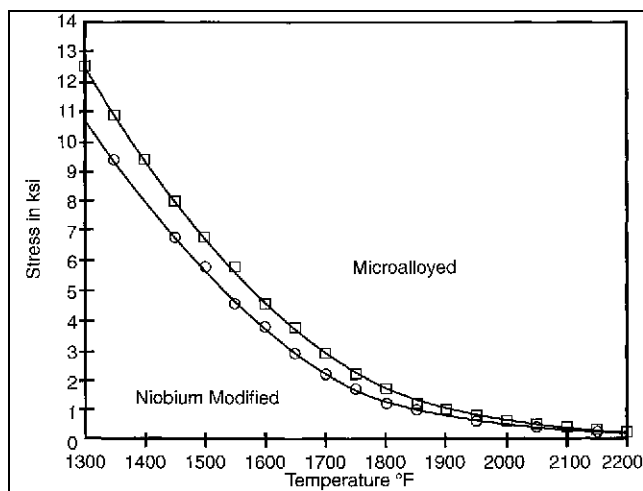
Figure 18 100,000 hour rupture strength of HP-high carbon vs same alloy with micro-alloying additions. Ref. 12
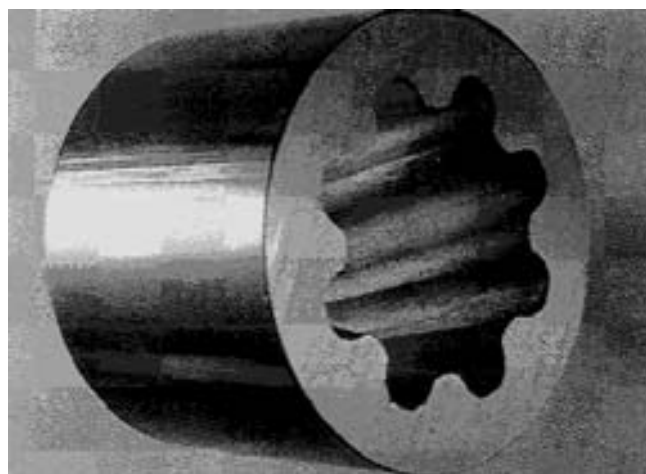
Figure 19 A section of wrought Inco Alloys 803 alloy with internal, spiralled fins. Tubes also are produced with straight fins by Inco and Sumitomo for newer, short residence time ethylene furnaces

wrought tubes. On the downside, these alloys do not appear capable of performing adequately at temperatures as high as the high carbon, highly alloyed cast tubes.

An interesting development is the internally finned tube pictured in *Figure 19*. Tubes in this configuration in Alloy 800H, Alloy 803, HK4M, and HPM are being used in ethylene service for radiant section cracking tubes. A typical 2 in.(51mm) outside diameter tube with a 0.236 (6mm) wall provides a 17% increase in ID surface area with addition of the fins. This increase in surface area increases thermal efficiency and allows shorter residence time.

The lower convection section tubes of ethylene cracking furnaces are usually Type 304H while the tubesheets that support them are static castings of HK-40 or, more likely, HP-Nb. Fittings such as elbows, return bends, etc. for use within the radiant and shield sections are static cast versions of the same alloy as the tubes. Outlet manifolds and other non-tubular components outside the firebox may be made in static castings of the low carbon alloys for easier fabricability or, if the temperature is low enough, the 20Cr-32Ni-Nb alloy may be used. Tubulars up to the quench point or the transfer exchanger are usually centrifugally cast in HP-Nb (high or low carbon) or 20Cr-32Ni-Nb.

Styrene Production

Styrene is one of many important derivatives of ethylene. Much of the equipment used in its manufacture operates at temperatures around 1200°F (650°C). This includes reactor reheaters and the piping and bellows connecting the reactor and the reheater. This equipment is usually fabricated of Alloy 800H. Up to one million pounds of Alloy 800H are used per year in the construction of styrene plants.

Failure of some Alloy 800 styrene plant components have been attributed to excessive retained stress, usually resulting from less-than-optimum fabrication practice. Elimination of this problem has been achieved by stress-relief annealing the fabricated parts prior to placing the unit in service.

Summary

Wrought and cast heat-resistant alloys are required in numerous refinery and petrochemical applications because of the combination of aggressive environments and strength requirements. High levels of nickel and chromium provide alloys with the capability of fulfilling these requirements on an economical basis. The alloys used for reformer tubing have been going through a transformation from HK-40 to HP-Nb for tubes and, more recently to the micro-alloyed grades. HK-40 was used almost exclusively for 20-25 years. There has been a similar evolution in the alloys used in ethylene furnaces which started earlier. The once commonly used wrought, heat resistant alloys were displaced almost completely by HK-40 which in turn has been displaced by HP-Nb. This evolution is continuing as reflected by the increasing use of the 35Cr-45Ni alloys. Some of the newer wrought alloys that have been introduced are now displacing the cast alloys in some niche applications (eg. short residence time ethylene cracking furnaces).

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