ACME® Heat Resistant Alloy Solutions for Steam Crackers
Steam Reformers (Catalyst Tube Assy.)
for Refining, Petrochemical Industry & DRI Plants
-Static & Centrifugal Cast Components
Refinery/Petrochemical Applications of Wrought and Cast Heat Resistant Alloys

Ni-Cr-Fe alloys are extensively used in refining and petrochemical plants equipments for both liquid and gaseous low temperature corrosion resistance and for heat resistant applications. In refining operations, most equipment operates below 260-316 °C (500-600 °F) is constructed of carbon steel or Cr-Mo-Fe alloys. An exception is the alkylation processes where highly alloyed materials are required to handle streams containing some sulphuric or hydrochloric acid. Other examples would be use of Type 316 and 317 for handling crude fractions with a high napthenic acid content and other higher alloys for flue gas desulphurization processes. Since petrochemical plants 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 316-538 °C (600-1000 °F), there is prominent 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. It is for equipment in services above 650 °C (1200 °F) 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, where they are used for tubes, hangers, supports, tube sheets and alike.

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

Notes on high temperature corrosion, and alloys used in steam-reformers & crackers

Today, energy costs and alloying element prices are high compared to 1970-1990. There has been a paradigm shift towards life cycle costing, and value analysis; while assessing a candidate alloy intended for use in a particular end application in any industry. Principle selection criteria applied to materials for refining and petrochemical plant equipment include- mechanical properties, corrosion resistance, and stability of properties, fabric-ability, availability and cost.

Because applications for heat resistant alloys involve thermal cycling, their thermal fatigue resistance is an important mechanical property that is considered during alloy selection. This property is a function of composition, but is also affected by section thickness and geometry. An example of this relationship is depicted in 180° return bends in ethylene cracking service. Some fitting designs include heavy outside wall to absorb erosion from coke particles. Such designs can suffer from thermal fatigue attributed to the cyclical nature of regular operations, de-cooking, and start-up and shut-downs. The figure at right exemplifies cracking that can eventually result.

Thinner, uniform wall tubes and similar components experiencing the same magnitude and frequency of cycles is not often observed in the industry. Moreover, through-wall cracking such as shown occurs infrequently. It is usually mitigated at about mid-wall as the probable result of the crack acting as a hinge.
There are inherent benefits of transition from SS310/HK/ HK-40/HK Modified (high Silicon / Nb), Alloy 800H to adopting modern practice of choosing HP-Modified/ HP-Micro Alloyed alloys for reformer applications.

For steam reformers the answer is the optimal combination of longer life and higher performance using thinner walls tubes. The higher strength of HP-Modified and HP-Micro alloy compared to HK-40 provide substantially longer stress-to-rupture life. HP-Modified enables operation with a thin-metal wall, which gives improvements in heat transfer rates and provides energy savings. In addition, newer designs now can utilize fewer tubes of a larger diameter thus saving tubing cost and furnace size.

In oxidizing environments (enrich with oxygen) most corrosion and heat resistant alloys rely on formation of an oxide film that renders corrosion resistance. Chromium oxide is one such generic oxide film formed on the surface of alloy. As temperature is increased the rate of oxidation also increases becoming deleterious. Higher chromium content is a common practice to achieve improved oxidation resistance.

Other elements including aluminium, silicon, and some rare earth elements are often added to enhance oxidation resistance.

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. 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 increases the metallurgy stability of the composition.

High temperature oxidation rates (shown in histogram at left) can vary significantly for quite similar centrifugally cast, modified HP heat resistant alloys. These alloys are commonly used in ethylene cracking and reformer furnaces.

For steam crackers savings accrue from combination of higher efficiency and production rates at higher temperature. Higher nickel content helps stabilize the austenitic structure and substantially improving carburizing resistance of the alloy either singly on its content or in conjunction with presence of silicon and aluminium, as shown in the graphic on the left.

Higher nickel content improves cyclical behaviour, the adherence of protective oxide films to the substrate, and the thermal fatigue properties due to changes in the stability of oxide films and diffusion process.
HP-Modified alloys contain between 0.40-0.50% carbon. This higher percentage of carbon is paramount, as it forms chromium carbides that combat metal deformation at elevated temperature service. Above 1000°C (1830°F) these carbides coalesce rapidly and therefore, decrease the creep rupture strength sharply. Addition of carbide-forming elements such as niobium (columbium), titanium, tungsten, and molybdenum are required to enhance creep strength at high temperatures.

**Carburization**

Carburization can occur when metals are exposed to carbon-monoxide, methane, ethane or other hydrocarbons at elevated temperatures. High temperature corrosion mechanism and phenomenon is similar in many ways to high temperature oxidation. Carbon from the environment combines with chromium and with other carbide forming elements - niobium, tungsten, molybdenum, titanium and alike, prominently known as carbide formers that are present in an alloy. Therefore, the nature and species of carbides can be a complex network of primary and secondary carbides in the alloy matrix. They form within the grains (secondary carbides embedded in primary carbides) and visible along the grain boundaries. Carbides are known to be hard, strong but brittle too. High brittle nature of carbides drastically lowers the ductility at elevated temperatures up to 482-538°C (900-1000°F). By keeping chromium locked up in the carbide matrix, lowers the available chromium required to withstand high temperature oxidation. Thus carburization also impedes elevated oxidation resistance in spite of being a chromium rich alloy. It also adversely affects creep strength and because of volume increase associated with the carbon uptake and carbide formation, it imposes additional stresses that contribute to mechanical failure. The stresses are evidences often by the localized bulging of tubes that are locally carburized. An example of carburization is shown below. A heavily carburized HP-Nb type tube with oxidation occurring at the chromium-depleted ID.

Carburization is uncommon in most refining operations because of the relatively low tube temperatures of mostly refinery fired heaters. However, it can and does occur in those elevated temperature processes heaters (for example cokers). It can also occur during an upset which results in the exposed material being heated to un-acceptably high temperatures. Where it is expected to occur within the range of operating conditions, it would be prudent to use Type 304H (higher carbon content 18Cr/8Ni) for temperatures up to about 816°C (1500°F).

There is no advantage of using either titanium or niobium stabilized grades since any un-reacted titanium or niobium from the original melt would be quickly tied up. Type 310 (19Ni-25Cr) or Alloy 800H (or equivalent) may be used for temperatures up to 1010°C (1850°F). For the most part, refinery application of latter two alloys for this purpose is limited to hydrogen reformer furnaces. Unfortunately, the 3xx series stainless steels including type 310, are subjected to sigma-phase embrittlement in the temperature range when have useful carburizing resistance. Alloy 800 H (or equivalents) would be a good choice in such cases.
The most effective element in mitigating and controlling carburization is nickel in combination with chromium. As earlier shown in figure; absorbed carbon, is plotted against nickel content with carbon absorption shown to decrease with increased nickel content. Silicon is another element, in conjunction with nickel is learnt to have a strong effect. This is one reason that in late 1970’s to early 80’s HK was modified with carbon 0.40% and then further with silicon contents 1%, 1.5% and 2% in practice. Aluminium in excess of 3.5-4.0% is also beneficial. Apparently, the presence of silicon in excess of 2% adversely affects the rupture strength and weld-ability of both wrought and cast heat resistant alloys. In particular, aluminium in concentrations higher than 2.0-2.5% has an adverse effect on ductility and fabric-ability of an alloy.

Many clients in refining and petrochemicals industry specified coatings or surface enrichment using silicon, aluminium, chromium and its various combinations which have been tried in attempt to control carburization of heat resistant alloys. These thermal barrier coatings (TBA), popularly known; have been unsuccessful for the long term. Agreeably, vapour diffused aluminium enrichment showed some promise and performed well at lower temperatures, but disintegrated after relatively short times at temperature above 1010-1040°C (1850-1900°F).

Carburization is a more prominent in petrochemical industry than refining. The most common incidences are in the radiant and shield sections of ethylene cracking furnaces. It is a major problem when tube temperatures escalate up to 1149°C (2100°F); and high carbon potential associated with the ethane, propane, naphtha, and other hydro-carbons feed stocks which are cracked. It occurs with less severity in reforming operations and in other processes handling hydrocarbon streams or certain ratios of CO/CO2/H2 gas mixtures at high temperatures. Even with the advent of HP-Mod alloys post 1980 period, carburization still remains a key reason demanding tube replacement. This is attributed to higher tube temperatures and severe operating conditions.

The rate of carburization of ethylene cracking tubes of a given alloy is “process driven”. As suggested earlier, temperature and carbon potential are primary factors that determine its rate. Increasing steam dilution will surely reduce the rate. The type of feed is also a factor with lighter feeds generally being more aggressive than heavier feeds owing to their higher carbon potential. Some operators prefer to pre-sulphide their coils while others use feedstock with crack able sulphur present or added. Eventually, this reduces catalytic characteristics of the tube surface and reduces coke formation. Therefore, further reduces the frequency of decoking which many believe to be paramount reason of carburization. Appropriate metallurgy of tubes can be used to reduce but rarely totally eliminate carburization.

Catalytic Steam Reformers for Hydrogen, Ammonia and Methanol Production

Catalytic steam reforming is a widely used process for the production of hydrogen for use in refinery hydrogenation process and the production of ammonia and methanol in the petroleum industry. Heat resistant alloys find wide use in reformer furnace that forms key component in the process. They are also widely used for other components from the primary reformer through the waste heat boiler. Operating temperatures of these components are in the range of 704-1010°C (1300-1850°F), at high pressures.

In most plants, methane is used feedstock. It reacts with steam in catalyst packed tube at high temperature which is a highly endothermic process. Typically the tubes have inside diameter of 60-120 mm (2-5 inch), and are 10-14 m (33-46 ft) long. The pressure is 15-30 bar (218-435 psi) and the temperature is between 900-1000°C (1652-1832°F). Tube wall thickness ranges from 8 to 20 mm (0.31-0.79 in) depending on tube diameter, temperature and pressure. Excess steam is used to reduce the formation of carbon. The reforming reactions are accelerated by high temperature but retarded by high pressure. A typical steam methane reformer for hydrogen and methanol production flow sheet is shown to the left.
Materials are required to possess good high temperature strength, ductility and thermal fatigue properties. Alloy 800 H/HT (and equivalents) has been used successfully for catalyst tubes, pigtails, header manifolds, high temperature transfer piping between primary and secondary reformers and for secondary reformers internals. Cast catalyst tubes are more prominent than Alloy 800 reformer furnaces. These are frequently made of centrifugally cast HK-40, HP-Nb or IN-519. Tube sheets and fittings and other components are made of these alloys in static castings. In general, HK-40 is being phased out in favour of HP-45 because of latter’s higher strength and superior 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. Importantly, thermal stress is reduced which helps in improving tube life. In addition, thermal efficiency is improved. HP-Nb alloy is widely used in ammonia reformer furnaces.

**Ethylene Cracking**

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

Most cracking furnaces have a configuration similar to that shown in figure to the right. Pyrolysis chemistry is aggressive and dictates not only the reactor design but also its operating practices and the design of its quench systems. Thermal cracking is non-catalytic process carried out above 1100°C (2012°F) and a few bar pressure. The disintegration of saturated hydrocarbon results in unsaturated light weight molecules of ethylene and propylene. The feedstock controls the primary and by-products. The cracking severity controls feedstock conversion. Selectivity is extremely important and is maximized by short residence time. There has been continuous evolution of designs to produce the optimum furnace.

Unlike reforming, pyrolysis does not employ large amounts of process steam, and therefore produces coke which accumulates in the reactor and must be removed in an off-line operation. The number of furnaces depends on plant capacity and feed stock.

In the past, ethylene yield improvements were obtained by raising the temperature and reducing the contact time (residence time) and pressure drop in the cracking coils. Plant experience reveals that a 100°C (212°F) increase in cracking temperature can increase the ethylene output by almost 50%! However, pyrolysis requires materials with high temperature strength and resistance to carburization. Carburization lowers ductility, making the tube more susceptible to stress damage either from thermal cycles or bending moments. This stressing of aged HK-40 components has resulted in many premature tube failures. Tube-to-tube interactions are attributed to variations in temperature (cycling or any other repeated pattern) and thermal expansion. Till the mid 1980’s and before, HK-40 was the most common tube material used in low-severity furnaces with 1000°C ( 1832°F) frequently considered as the upper limit. Several problems arose because of lack of ductility, carburization and low-cycle fatigue (LCF).

In high severity furnaces today, tube skin temperatures of 1025°-1150°C (1877-2102°F) are reached. Key to succeed in such applications is use of a high-strength alloy with superior carburization resistance with capability to regenerate its protective oxide film during de-coking; good creep-rupture properties without excessive creep and distortion (lengthening and blowing of tubes) and ability to handle cycling conditions (low cycle fatigue). There are several HP-Mod alloys capable of meeting these demanding requirements.
As the strength at these elevated temperatures is limited for all Fe-Cr-Ni and Fe-Ni-Cr alloys, resistance is related in part to the nickel and silicon contents. Chart on the left ranks a number of alloys with regard to carbon absorption. Chart below shows how carburization rates almost doubles every 38°C (100°F) rise in temperature and can become very severe above 1050°C (1922°F).

HP-Mod alloys have gained recognition and acceptance because of their good carburization and oxidation resistance at elevated temperature service. Microalloying and intelligent additions of tungsten, titanium, and niobium/columbium prominently to carburization.

Though carburization is a major factor, final failures are generally caused by creep rupture. Creep can affect coil systems by relaxing induced stresses, by distorting the piping configuration, thereby cause a creep rupture mechanism failure. Stress relaxation due to creep is beneficial because it prolongs service life of tubes. But when creep results in distortion in the furnace tubing configuration, it can have detrimental effect as it can upset the balance between the support forces and pipe weight. Therefore, an optimal compromise is sought between creep rupture strength and creep ductility. Sufficient ductility implies capability of handling thermal shock as well as thermal fatigue due to aging and cycling between pyrolysis cracking and de-coking operations, and as a result of start-up and shut-down.

HP-Mod alloys are successfully used for operations up to 1150°C (2102°F) and the modified 28/48 W alloys up to 1200°C (2192°F). Some HP-Mod alloys contain cobalt, which can be considered in Ni to the Cr-Ni ratio, as behaviour of cobalt is similar to that of nickel.
The shield section, the lower convection section, the outlet transfer line and the quench unit of ethylene cracking furnaces generally operate at significantly lower temperatures but also must be made of heat resistant alloys. For tube and other support components, Alloy 800, 253MA and equivalents have been used successfully up to 1010-1038°C (1850-1900°F). However, radiant and shield tubes more often use the centrifugal cast modified HP-family alloys—even at lower temperatures. Most prominent amongst them is the HP-Nb modified. Others that are used are alloyed with other carbide forming elements and solid solution strengtheners such as molybdenum and tungsten.

Newer metallurgical developments are grades that are referred as “MA-micro alloyed”, that contain small (trace) amounts of titanium, zirconium and rare earth metals (REM). The micro-alloy additions enhance the tube metallurgy, with improved stress-rupture properties which is attributed to development of finer, more dispersed carbides rather than being present in clusters. The rare earth addition further improves adhesion of protective oxide film for longer duration time to the base alloy surface, thereby improving oxidation resistance and carburization resistance at elevated temperatures. The effectiveness of micro-alloying is dependent on the melting and pouring practice. Total de-oxidation of melt is a desideratum for consistent and improved performance.

Majority of the cast alloys have a carbon content of 0.40-0.50% but there have been low carbon 0.10-0.18% variants produced for use as sweep bends in some of the short residence time’s furnaces using smaller diameter tubes (≈ 38-65 mm internal diameter) to improve ethylene yield. Lately, some operators have begun to use higher nickel-chromium (35Cr-45Ni) alloys for their higher temperature operations.

The lower convection section tubes of ethylene cracking furnaces are usually of Type 304H while the tube sheets and tube supports which them are static castings of HK-40, HK-40 Modified (Si 2%), or more likely HP-Nb. Fittings such as elbows, return bends, weldolets etc. For use within the radiant and shield sections are static cast versions of the same alloy as the tubes. Outside manifolds and other non-tubular components outside the firebox may be made of static castings of the low carbon alloys for easier fabric-ability. If temperatures are low enough, the 20Cr-32Ni-Nb/Cb alloy may be used.

ACMECAST® offers wide range of low and high carbon heat resistant alloys conforming to ASTM, DIN and alike specifications along with proprietary modifications of silicon, niobium/columbium, titanium, cobalt, tungsten, and rare earth elements (REM) micro-alloyed.

Tubulars up to the quench point or the transfer exchanger are usually centrifugally cast in HP-Nb/Cb (high or low carbon) or 20Cr-32Ni-Nb/Cb.
Definition and Alloy Classification of Heat Resistant Alloys

Cast heat-resistant alloys are primarily used in applications where service temperature exceeds 650°C (1200°F) and may reach as high as 1315°C (2400°F). Strength at elevated temperatures is often key consideration in alloy selection however the resistance of an alloy to attack by the environment, present of aggressive corrodants, and the imposition of cyclic stresses and temperatures are some other important factors that may need equal consideration.

Several cast heat-resistant alloys are in composition related to the wrought stainless steels and to the cast corrosion-resistance stainless steels as shown in Table 1.0. Reference to wrought corrosion resistant stainless steels and heat resistance stainless steels most often made by purchasers, and end users; owing to ease of availability and identification.

<table>
<thead>
<tr>
<th>Cast Heat-Resistant Grade</th>
<th>Wrought Corrosion-Resistant Stainless Grade</th>
<th>Cast Corrosion-Resistant Stainless Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>446</td>
<td>CC50</td>
</tr>
<tr>
<td>HD</td>
<td>327</td>
<td></td>
</tr>
<tr>
<td>HE</td>
<td>312</td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>302B</td>
<td>CF20</td>
</tr>
<tr>
<td>HH II</td>
<td>309</td>
<td>CH20</td>
</tr>
<tr>
<td>HK</td>
<td>310</td>
<td>CK20</td>
</tr>
<tr>
<td>HT</td>
<td>330</td>
<td></td>
</tr>
</tbody>
</table>

The major difference between these materials is their carbon content. With a few exceptions, carbon in the heat-resistant alloys lie in range of 0.30 to 0.60% compared with 0.01 to 0.25% carbon normally associated with the wrought- and cast-corrosion resistant grades. In addition, there is difference in percentage of manganese and silicon, with cast heat-resistant alloys possessing higher percentage compared to wrought- and cast- corrosion resistant grades. Such key difference in percentage of carbon, manganese and silicon results in significant changes in the alloy properties. For example, the higher rupture strength of the cast alloys, which are compared with those of wrought alloys in Table 2.0. It is therefore, important to recognise these distinctions, because each group of alloys has its own appropriate application and related specifications.

<table>
<thead>
<tr>
<th>Form</th>
<th>Alloy</th>
<th>10,000 hour rupture strength ksi</th>
<th>10,000 hour rupture strength ksi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrought</td>
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<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Cast</td>
<td>HH II</td>
<td>1.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Wrought</td>
<td>310</td>
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<td>0.5</td>
</tr>
<tr>
<td>Cast</td>
<td>HK 40</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Wrought</td>
<td>330</td>
<td>0.6</td>
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</tr>
<tr>
<td>Cast</td>
<td>HT</td>
<td>1.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

A wide range of cast heat-resistant alloys have been developed to meet varied industrial needs. The composition of these alloys is mentioned in Table 3.0. The standard grades, which are recognized by ASTM specifications, fall in a range from 0 to 68% nickel with 8 to 32% chromium and the balance primarily iron plus up to 2.5% silicon and 2% manganese.

Higher carbon content in the range of 0.40-0.50% has its metallurgical significance in reformer applications. Although in the reformer business HP-Mod is generally understood as 25Cr-35Ni-1Nb-0.4C, in the ethylene market its is construed as a range of HP-Mod alloys, confirming to American Society of Testing Standard) ASTM A 297 / A 297M Grade HP alloys, with a restricted carbon range and additions of niobium (columbium), niobium and tungsten, tungsten and molybdenum represented as HP-40 Mod Nb, HP-40-Mod Nb W, HP-Mod W and alike. HP-45 designates mid-carbon range, nonetheless, HP-10 Mod Nb is increasingly used in the ethylene market for its excellent balance of strength and ductility. Modern HP modified alloys include additions of Rare Earth Metals (REM) like zirconium, cerium, yttrium, with micro-alloying with aluminium and titanium. Fewer alloys contain more than 30% chromium.
Table 3.0 ASTM Standard Designations and Compositions of Cast Heat-Resistant Stainless Steels—Composition (% w/w)

<table>
<thead>
<tr>
<th>Alloy Grade</th>
<th>ASTM Specification</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo*</th>
<th>Nb/Cb</th>
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<td>HA</td>
<td>1,2,3</td>
<td>0.20</td>
<td>0.35-0.65</td>
<td>1.0</td>
<td>0.04</td>
<td>0.04</td>
<td>8-10</td>
<td>-</td>
<td>0.9-1.2</td>
<td>-</td>
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<tr>
<td>HC</td>
<td>1,3</td>
<td>0.50</td>
<td>1.0</td>
<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
<td>26-30</td>
<td>4</td>
<td>0.50*</td>
<td>-</td>
</tr>
<tr>
<td>HD</td>
<td>1,3</td>
<td>0.50</td>
<td>1.5</td>
<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
<td>26-30</td>
<td>4-7</td>
<td>0.50*</td>
<td>-</td>
</tr>
<tr>
<td>HE</td>
<td>1,3</td>
<td>0.2-0.5</td>
<td>2.0</td>
<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
<td>26-30</td>
<td>4-7</td>
<td>0.50*</td>
<td>-</td>
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<td>0.2-0.4</td>
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<td>0.04</td>
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<td>8-12</td>
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<td>2.0</td>
<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
<td>24-28</td>
<td>11-14</td>
<td>0.50*</td>
<td>-</td>
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<tr>
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<td>0.2-0.5</td>
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<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
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<td>1,3,5</td>
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<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
<td>24-28</td>
<td>18-22</td>
<td>0.50*</td>
<td>-</td>
</tr>
<tr>
<td>HL</td>
<td>1,3</td>
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<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
<td>28-32</td>
<td>18-22</td>
<td>0.50*</td>
<td>-</td>
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<tr>
<td>HN</td>
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<td>0.2-0.5</td>
<td>2.0</td>
<td>2.0</td>
<td>0.04</td>
<td>0.04</td>
<td>26-30</td>
<td>14-18</td>
<td>0.50*</td>
<td>-</td>
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<tr>
<td>HP</td>
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<td>2.0</td>
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<tr>
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<tr>
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<td>0.04</td>
<td>0.04</td>
<td>15-19</td>
<td>64-68</td>
<td>0.50*</td>
<td>-</td>
</tr>
<tr>
<td>CT15</td>
<td>5</td>
<td>0.05-0.15</td>
<td>1.5</td>
<td>1.5</td>
<td>0.03</td>
<td>0.03</td>
<td>19-21</td>
<td>31-34</td>
<td>0.50*</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>50-50-Nb</td>
<td></td>
<td>0.10</td>
<td>0.3</td>
<td>0.5</td>
<td>0.02</td>
<td>0.02</td>
<td>47-52</td>
<td>Bal</td>
<td>-</td>
<td>1.4-1.7</td>
</tr>
</tbody>
</table>


*Mo optional

Alternate Classification

An alternative method of classification is based on the order of the diminishing quantity of major elements. It comprises of following four groups:

1. Iron-Chromium (Fe-Cr) HA, HC, HD
2. Iron-Chromium-Nickel (Fe-Cr-Ni) HE, HF, HH, HI, HK, HL
3. Iron-Nickel-Chromium (Fe-Ni-Cr) HN, HP, HT, HU
4. Nickel-Iron-Chromium HX, HW

Proprietary and Semi-Proprietary Grades

Many of the proprietary alloys or proprietary compositions that are now in public domain can be classified broadly into three groups, with the following base compositions:

- 20Ni-25Cr
- 35Ni-25Cr
- 45Ni-30Cr

ACME® Modified & Proprietary Grades

Fundamental requirements in increasing high temperature capability include increase in strength at elevated temperature and increase in environmental resistance. Thus, in many cases the overall design requirement cannot be satisfied by a single material. Coatings are commonly required. Depending on the complexity of the component duty it may be necessary and in extreme cases, to apply multiple coatings to protect against different environmental factors, for example- corrosion, abrasion, impact and wear.
The various complementary mechanisms which strengthen metallic materials and increase temperature capability include solid solution strengthening and dispersion strengthening. They all operate by making dislocation movement more difficult. Solid solution strengthening is applicable to all base metals. Precipitation hardening is a potent strengthening mechanism but is limited to certain alloy types. Dispersion strengthening using fine dispersion of stable particles can be effective in developing strength at very high temperatures.

Grain boundaries play a very significant role in relation to material strength. Depending upon temperature, they can be beneficial and play a role in increasing strength or can be detrimental and reduce strength. Thus, the grain size may be controlled within specified limits, the behaviour of grain boundaries may be modified and the boundaries themselves may be eliminated through the use of components in the form of single crystals.

**Solid Solution Strengthening**

When atoms of one metal are substituted into the crystal lattice of another metal, internal strains are generated, resulting in strengthening. The extent of strengthening produced depends on the atoms involved. Atoms with similar crystal structures and lattice parameters will have high mutual solubility and with generate relatively little strengthening. Atoms of different size may have limited solubility but could potentially generate significant strengthening.

The effect of various alloying elements—tungsten, molybdenum, vanadium on the proof stress of gamma iron is buttressed by considerable research and as in case with alpha iron, the interstitial atoms N and C are more effective than the substitutional atoms.

Tungsten and molybdenum have long been recognized as strong solid solution strengthening elements in nickel super alloys. Recently, rhenium has been found to be a particularly effective element, partitioning mainly to the matrix, reducing diffusion rates and therefore retarding coarsening of the gamma precipitate. It also forms short range ordering with very small clusters of atoms in the matrix, which act as effective obstacles to dislocation movement.

**Grain Size and Grain Boundary Effects**

A grain boundary is a region of mismatch between the lattices of adjacent grains. The effect of the grain boundary on properties varies with temperature. At temperatures up to around 50% of the melting temperature the boundary impedes dislocation movement and thus provides a strength-mechanism. At higher temperatures, diffusion becomes increasingly important and is much more rapid in the grain boundaries than within the grain. Grain boundaries are therefore sources of weakness in high temperature creep processes. Depending on the service temperature of the component, the grain size and shape can be controlled, and the grain boundary structure can be modified, to optimize properties.

**ACME® offers proprietary alloys and modifications of standard alloy grades, that involve strengthening of the alloy solid solution with single or multiple additions of the elements aluminium, molybdenum, niobium, rare earth metals (REM)-Ce, La, Ta, Re, Y, titanium, tungsten and zirconium are added to improve specific properties; such as high-temperature strength, carburization resistance, and resistance to thermal cycling and fatigue.**

Research reveals that in Fe-Ni-Cr and Nickel Base Alloys following objectives can be achieved with element alloying additions:

- **Solid solution strengthening**: Mo, Ta, W, Re
- **Precipitation strengthening**: Al, Ti, Ta
- **Grain boundary strengthening**: B, C, Zr, Hf
- **Surface protection**: Al, Cr

**Reference Literature & Content Source**

- NDI Technical Series: 9021, 10001, 10017, 10022, 10031, 10032, 10010, 10058, 10059, 10071, IN-519
- ASM Specialty Handbooks: Stainless Steels, Nickel & Cobalt Base Alloys; Shrier’s Corrosion # 1: High Temperature Corrosion
- Niobium: High Temperature Applications (TMS Publication), ASM -High Temperature Property Data: Ferrous Alloys
Custom Made - Components for Steam Reformers and Steam Crackers (Catalyst Tubes)

Manufactured Alloy Range

USA Standard Specification
- ASTM A 297 – Grade HF, HH, HK, HP, HT, HW, HX
- ACME® Modified Versions
  - Mo, Ti, Nb/Cb, W, Rare Earth Metal (REM)
- ASTM A 477– Type I, Type II
- ASTM A 560: 50Cr-50Ni, 50Cr-50Ni-Nb/Cb
- ASTM A 1002 (New Standard): Ni-Cr Ordered Alloy for service up to 1250°C

ACME® Modified Heat Resistant Alloys
- ACME® HP-Rare Earth Metal (REM)
- ACME® HP-45
- ACME® HP-45-Nb/Cb
- ACME® HP-Nb-W
- ACME® HP-45-Mo
- ACME® HK-40
- ACME® 50Cr-50Ni-Nb/Cb
- ACME® 45Ni-35Cr-REM

DIN Heat Resistant Alloys
- 1.4826  GX40CrNiSi 22-9
- 1.4832  GX25CrNiSi 20-14
- 1.4837  GX40CrNiSi 25-12
- 1.4840  GX15CrNi 25-20
- 1.4848  GX40CrNiSi 25-20
- 1.4849  GX40NiCrSiNb 38-18
- 1.4852  GX40NiCrSiNb 35-25
- 1.4855  GX30CrNiSiNb 24-24
- 1.4857  GX40NiCrSi 35-25
- 1.4859  GX10NiCrNb 32-20
- 2.4680  G-NiCr50Nb

Components for Steam Reformers (Catalyst Tubes)
- Tube supports
- Hangers
- Inlet and outlet manifolds
- End caps
- Reducers-concentric/eccentric
- Y-pieces
- T-pieces
- Catalyst grid plates
- Reformer tubes* –centrifugal cast
- Thermo wells
- Flanges
- Fittings
- Weldolets
- Riser tubes *

Components for Steam Crackers
- Elbows
- Tube sheets*
- Centrifugal cast tubes*
- Thermo-wells
- U-Bends
- 180° Return bends
- Weldolets
- Y-pieces
- Burner spares
- Plug headers
- Flanges
- Fittings
- Fasteners

** Static Cast Radiant Tubes up to 4” diameter -1500 mm single piece

(∗) Centrifugal Cast Tubes From associate source
Talk to us of your end application(s) requirements, new projects or plant’s maintenance needs.

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