Factors affecting material selection for high temperature applications - review

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Keywords

heat resisting steels, microstructure, material selection, embrittlement, sigma phase, carbide, grain growth

Abstract

Stainless steels are most commonly selected for their aqueous corrosion resistance, but are also widely used at elevated temperatures when carbon and low-alloyed steels do not provide adequate corrosion resistance and/or sufficient strength. They can be found in applications in which high temperature oxidation resistance is necessary and in others in which high temperature strength is required. There is a variety of factors affecting material selection for high temperature applications and a wide range of steel grades available, starting with corrosion resistant grades to special steel grades developed for particular application. The focus will be given to “workhorses” used at high temperatures. Mechanisms of microstructure changes, embrittlement, softening and mechanical properties at high temperatures are discussed.

1 Introduction

In many industrial, as well as public and domestic applications, the construction material is exposed to elevated temperatures, sometimes in connection with a more or less aggressive environment.

Depending on the operating conditions, the demands on material used at elevated temperatures may be as follows:

- high creep strength (and/or ductility)
- high resistance to oxidation and high temperature corrosion
- stability of microstructure
- good resistance to erosion-corrosion

All material selection should be defined by the application and operating conditions in each individual case (1). Knowledge of possible microstructure changes, embrittlement and high temperature mechanical properties is of great help and could
prevent possible unexpected failures in the process. Material selection process should not be underestimated when trying to identify an optimum grade for an application.

2 The role of alloying elements

Alloys intended for high-temperature applications are designed to have the capability of forming protective oxide scales. The only oxides that effectively meet the criteria of protective scales and can be formed on practical alloys are chromium oxide (Cr$_2$O$_3$), aluminium oxide (Al$_2$O$_3$) and possibly silicon dioxide (SiO$_2$).

The effect of chromium is particularly evident at temperatures above 500 °C. This element forms a tight, adherent layer of chromium-rich oxide on the surface of the metal,retarding the inward diffusion of oxygen and impeding further reaction (2).

Other elements besides chromium may also be added to stainless steel to increase oxidation resistance. Silicon and aluminium act very similarly to chromium. They are oxidised selectively and if present in sufficient amounts, can form continuous films of SiO$_2$ and Al$_2$O$_3$. The adherence of the oxide scale can be greatly improved by small additions of rare earth metals (REM) like cerium or lanthanum (3). This is particularly beneficial when the application is subjected to thermal cycling (4).

Nickel increases ductility, high temperature strength and resistance to both carburisation and nitridation. High nickel alloys should be avoided in reducing sulphidising environments, since the formation of low melting point nickel-sulphur compounds. Nickel counteracts, but does not necessarily stop, the tendency for an alloy to form sigma phase.

Higher nitrogen and carbon content enhance creep strength.

Molybdenum increases high temperature creep-rupture strength. The content of molybdenum is mostly limited to 3.0 %. With higher molybdenum content serious oxidation problems can occur. It promotes sigma phase formation, unless it is counterbalanced by austenite forming elements, such as nickel.

Titanium is added in small amounts, about 0.3–0.7 % and increases strength in austenitic alloys. The same is true also for niobium. They both promote sigma formation.

Boron increases creep-rupture strength and is used at rather low concentrations, 0.002 % is typical. Boron is an interstitial element and tends to concentrate at the grain boundaries.
3 The role of microstructure

Microstructure is less important for heat resistance than chemical composition or the appropriate selection of alloying elements, but has an influence on the suitability for high temperature service due to other reasons. The grades of wrought stainless steels and nickel-base alloys being usually employed for products, for which the main requirement is their resistance to the effect of hot gases and products of combustion at temperatures above 550 °C are specified in European standard EN 10095 – Heat resisting steels and nickel alloys (5). This standard comprises six ferritic grades, fourteen austenitic heat resisting and one duplex heat resisting grade.

For most ferritic grades the long term service temperature is usually limited to 250 °C, because of 475 °C embrittlement. This phenomenon does not seem to be a serious problem in the low chromium steel grades with 10.5–12.5 % Cr, which have been extensively used in automobile exhaust systems, where temperatures can exceed 575 °C, at times. A contributory reason is that 475 °C embrittlement can be reversed by heat treatment at higher temperatures. The resistance to atmospheric corrosion and high temperature oxidation at relatively low cost are the reasons why some ferritic grades have been used extensively in automotive exhaust systems (6). Another exception to the maximum service temperature limit are high-alloyed chromium steel grades with 23–27 % Cr, which offer outstanding scaling resistance in air at high temperatures because of their high chromium content.

Martensitic stainless steels are listed in the European standards EN 10088-1 (7) and EN 10302 as creep resisting steels (8). However, due to their low chromium content of 12.5 % maximum, they are specified not primarily as heat resisting grades. They are mostly used when the application requires good tensile strength, creep and fatigue strength properties, in combination with moderate corrosion resistance and heat resistance up to approximately 650 °C. Low and medium carbon martensitic steels have been used primarily in steam turbines, jet engines and gas turbines.

Austenitic stainless steels provide next to nickel-base alloys, the best combination of high temperature corrosion resistance and high temperature mechanical strength of any alloy group. For this reason there is a multitude of special heat resisting austenitic grades listed in EN 10095 and of special creep resisting austenitic grades listed in EN 10302. The heat resisting austenitic grades are the preferred metallic material in construction of high temperature applications.
Duplex stainless steels have yield strength in the range from 550 MPa to 690 MPa in the annealed condition and this is significantly higher than their austenitic or ferritic counterparts. Despite this relatively high strength at room temperature, duplex grades are subject to embrittlement and loss of mechanical properties, particularly toughness, through prolonged exposure to high temperatures. As a result, duplex stainless steels are generally not recommended for elevated-temperature applications and their upper temperature limit is usually not higher than approximately 300 °C.

Grades primarily designed for aqueous corrosion resistance may also be used as heat resisting steel grades, if corrosion resistance is of high importance. These steel grades are listed in EN 10088-1 and EN 10028-7 (10) and provided below in Table 1.

Table 1: Grades from EN 10088-1 and EN 10028-7 which are used in addition to those in EN10095 as heat-resistant steels

<table>
<thead>
<tr>
<th>Steels from EN 10088-1</th>
<th>Steels from EN 10028-7</th>
<th>Approximate AISI/ASTM designations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Number</td>
<td>Name</td>
</tr>
<tr>
<td>X2CrTi12</td>
<td>1.4512</td>
<td>X3CrTi17</td>
</tr>
<tr>
<td>X6CrTi13</td>
<td>1.4000</td>
<td>X2CrTi17</td>
</tr>
<tr>
<td>X6Cr17</td>
<td>1.4016</td>
<td>X2CrTi17</td>
</tr>
<tr>
<td>X3CrTi17</td>
<td>1.4510</td>
<td>X2CrTi17</td>
</tr>
<tr>
<td>X2CrNbZr17</td>
<td>1.4590</td>
<td>X2CrTi17</td>
</tr>
<tr>
<td>X2CrTiNb18</td>
<td>1.4509</td>
<td>X2CrTi17</td>
</tr>
<tr>
<td>X12Cr13</td>
<td>1.4006</td>
<td>X2CrTi17</td>
</tr>
<tr>
<td>X5CrNi18-10</td>
<td>1.4301</td>
<td>X5CrNi18-10</td>
</tr>
<tr>
<td>X6CrNi18-10</td>
<td>1.4948</td>
<td>X5CrNi18-10</td>
</tr>
<tr>
<td>X6CrNiTi18-19</td>
<td>1.4541</td>
<td>X6CrNiTi18-19</td>
</tr>
<tr>
<td>X7CrNiTiB18-10</td>
<td>1.4941</td>
<td>X6CrNi18-10</td>
</tr>
<tr>
<td>X6CrNi23-13</td>
<td>1.4950</td>
<td>X6CrNiTi18-19</td>
</tr>
<tr>
<td>X6CrNi25-20</td>
<td>1.4951</td>
<td>X6CrNi23-13</td>
</tr>
<tr>
<td>X2CrNiN23-4</td>
<td>1.4362</td>
<td>X2CrNiN23-4</td>
</tr>
</tbody>
</table>
The temperature range where the above stainless steel grades are used is somewhat lower than for the steel grades specifically designed and listed as heat-resistant grades. It should be borne in mind that maximum service temperature is different depending on intermittent or continuous service.

### 4 Stability of microstructure

With time and temperature, changes in metallurgical structure can be expected with any metal. In stainless steel, the changes can be softening, carbide precipitation or embrittlement (9). Some materials change after a few hundred or thousand hours in service. They become brittle instead of remaining tough and ductile. The most common problem is that the alloy forms a hard, brittle non-magnetic phase, called sigma. Sigma phase forms in the temperature range of 500–980 °C. Embrittlement due to sigma phase starts rapidly if the material has been cold worked. Sigma phase may not seriously harm the alloy while it is operating at high temperature, but enough sigma phase can completely embrittle the alloy when it reaches room temperature (11). This microstructural change can occur in austenitic, ferritic or duplex stainless steel and the process is dependent on both time and temperature. Some of the lower chromium alloyed ferritic grades can form sigma phase at temperatures as low as 480 °C, albeit over extended periods of time.

In addition to temperature, the time required to form sigma phase varies considerably depending on composition and processing (the amount of cold working, for example). With a sufficiently high level of nickel, sigma phase formation can be suppressed.

Other intermetallic phases very often present beside sigma phase are Laves and chi ($\chi$) phases. In the case of Laves phase, such intermetallics can even improve high-temperature creep strength.

Diffusion of carbon in stainless steel results in the formation of additional carbides. With the carburisation massive carbides are formed in the austenite matrix. The primary significance of carburisation is its effect on properties. A carburised alloy has slightly increased creep strength and a change in volume results from the increased amount of carbide with a lower density than that of the original alloy. The original alloy and carburised layer are different in density and coefficient of thermal expansion. During thermal cycling, these differences promote the generation of high thermal stresses that can result in failure at elevated temperatures. With this process the oxidation attack is also promoted by the depletion of chromium from the matrix.
Table 2: Practical considerations of structure stability in use (12, 13, 14)

<table>
<thead>
<tr>
<th>Steel designation</th>
<th>Most suitable temp. range</th>
<th>Max. recommended service temperature in dry air (°C)</th>
<th>Exposure time$^{1)}$</th>
<th>Embrittlement effect</th>
<th>475 °C embrittlement</th>
<th>Grain boundary carbides</th>
<th>α-phase</th>
<th>Grain growth</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>Name</td>
<td>Nearest ASTM/AISI</td>
<td></td>
<td></td>
<td>600-750 °C</td>
<td>600-900 °C</td>
<td>&gt; 950 °C</td>
<td>&gt; 1050 °C</td>
<td></td>
</tr>
<tr>
<td>1.4818</td>
<td>1.4828</td>
<td></td>
<td>1000</td>
<td>Short Long Medium</td>
<td>Low</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4833</td>
<td>X12CrNi23-13</td>
<td>309S</td>
<td>1000</td>
<td>Long Medium</td>
<td>Low</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4835</td>
<td>X9CrNiNISCe21-11-2</td>
<td>S30815</td>
<td>850-1100</td>
<td>Long Medium</td>
<td>Low</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4841</td>
<td>X15CrNiSi25-21</td>
<td>314</td>
<td>1150</td>
<td>Medium /strong</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4845</td>
<td>X8CrNi25-21</td>
<td>310S</td>
<td>1100</td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4854</td>
<td>S35315</td>
<td>1150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4878</td>
<td>X8CrNiTi18-10</td>
<td>321H</td>
<td>800</td>
<td>Long Medium</td>
<td>Low</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4948</td>
<td>304H</td>
<td>800</td>
<td>Short Long Medium</td>
<td>Low</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4713</td>
<td>X10CrAl7</td>
<td>550-800</td>
<td>800</td>
<td>Low</td>
<td></td>
<td></td>
<td>No brittle phases, but should be exposed to only moderately corrosive atmospheres</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4724</td>
<td>X10CrAl13</td>
<td>550-850</td>
<td>850</td>
<td>Low</td>
<td></td>
<td></td>
<td>No brittle phases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4742</td>
<td>X10CrAl18</td>
<td>550-1000</td>
<td>1000</td>
<td>Medium</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>1.4762</td>
<td>X10CrAl24</td>
<td>550-1150</td>
<td>1150</td>
<td>Medium, but higher than 1.4742</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>α-phase after long exposures, but faster than 1.4742 grain growth</td>
</tr>
</tbody>
</table>

$^{1)}$ short=seconds-minutes, medium=minutes-hours, long=days-months
Grain growth may also occur, possibly increasing the creep strength somewhat, but simultaneously reducing the ductility substantially. Even if these microstructural changes lead to impaired material properties, they can be acceptable as long as one is aware of them and considers them during service as well as at maintenance shutdowns (1).

At temperatures between 400 °C and 500 °C the ferritic stainless steels tend to split into two separate phases, with respectively high and low chromium contents. The rate of the reaction reaches the maximum at 475 °C. The 11 % Cr ferritic grades are least sensitive to this phenomenon, which occurs only to a limited extent in 17 % Cr alloys, whereas the 25 % Cr materials, including duplex stainless steels, are highly prone to it (15).

5 Operating conditions

Technical data illustrating the properties of heat-resistant alloys are very helpful in the selection of an alloy suitable for a given application. However, the long-term exposure to different environments and temperatures can neither be completely documented nor described by laboratory tests. Experiences obtained from many actual installations are most helpful. One must develop the judgement needed to determine which of the many factors involved are the most important.

Temperature is often the first – and sometimes the only – data point given in the alloy selection, but a successful material selection cannot be based on temperature only. The first step in material selection is to know the maximum temperature at which a given alloy may have useful long term engineering properties.

When we work in vacuum metal loss form oxidation cannot occur. Therefore rather lean alloys may be used to extreme temperature if mechanical properties suit.

The alloys performing well in plain hot air are also suited for oxidising products of combustion of natural gas and even coal. Generally, oxidation and strength are the only issues. "Oxidation" usually refers to metal wastage, but concern about product contamination from scale is an occasional issue (11).

Combustion of fossil fuels, biofuels or waste produces gases with various contents of aggressive impurities. The least contaminated fuel is natural gas, the combustion products of which are mainly carbon monoxide, carbon dioxide and water. It may contain minor amounts of sulphur. The reduction in maximum service temperature compared to pure air exposure is modest, approximately 50–100 °C. Sulphur is more abundant in coal and oil. In addition, coal contains chlorine, while rather high levels of vanadium can be found in oil. The impurity levels vary according to the grade and origin of the fuel and can lead to more than 500 °C of reduction in maximum service temperature, compared to service in air.

Applications with reducing gases are not very common, the main exception is the bright-annealing of steel, in which a reducing atmosphere is used to prevent
oxidation and to "dissolve" existing oxide scales. In reducing atmospheres, which occur in certain areas of the current generation of low-NO\textsubscript{x} burners, sulphidation from both coal and oil fuels can be a serious matter. In such cases nickel content of the alloy should be kept to about 20 \%, to minimise sulphidation attack.

6 Conclusion

Material selection for high-temperature service is a complicated task and should not be lightly or inexpertly undertaken. The ideal alloy that will satisfactorily fill all of every designer's need, will never be discovered (2).

The very complex nature of high-temperature corrosion and the lack of standardised testing practices make it virtually impossible or at least not meaningful to present corrosion data in tables.

When choosing material for high-temperature applications, one must have an extensive knowledge of existing or expected service conditions, such as service temperature, gas composition and material temperature, time at temperature, vibrations, etc. Knowledge of previously used materials, their service performance and the cause(s) of previous failures is usually of great help in the process of material selection when trying to identify an optimum grade (16).

7 Literature

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