Materials selection considerations for thermal process equipment

Alloy selection criteria for high temperature service should include consideration of mechanical properties at temperature, resistance to oxidation or hot corrosion, and availability. Design of equipment can be just as important as the choice of material. Technical data illustrating the properties of heat resistant alloys are very helpful guides in selecting an alloy suitable for a given application. However the behavior of alloys during long exposure to the many environments and temperatures that may be encountered cannot be completely documented nor described by laboratory tests. Experience obtained from many actual installations is helpful in developing the judgment needed to determine which of the many factors involved are the most important.

Bryan Peters
Rolled Alloys Ltd.,
Blackburn (UK)

Tel. +44 (0)1254 / 582999
Email: blackburn@
rolledalloys.de

James Kelly
Rolled Alloys Ltd.,
Michigan (USA)

Tel. +1-734-8470561
Email:
sales@rolledalloys.de

Jason Wilson
Rolled Alloys Ltd., Breda
(Netherlands)

Tel. +31 (0)76 / 5489899
Email: sales@rolledalloys.de

A few points to consider

Temperature

Temperature is often the first—and sometimes the only—data point given when we are asked for suggestions regarding alloy selection. One cannot successfully choose an alloy based on temperature alone. Nevertheless, a simple first guide to alloy selection is to at least know the very maximum temperature at which a given alloy might have useful long term engineering properties. Considering oxidation as the limiting factor one might rate alloys as follows, in plate form, 5 mm and over. Remember that thin sheet will have a lower limiting temperature due to proportionally greater losses from oxidation:

- Carbon steel, such as ASTM A 387 Grade 22 (2 1/4Cr, 1Mo). Useful strength to 650°C. Above 510°C 304H is stronger and, of course, more oxidation resistant.
- 410 and 410S stainless, 1.4000, 1.4024. Limited by oxidation to 650°C. Subject to embrittlement after several years' service above about 315°C.
- 304/304H & 316 stainless. 1.4301, 1.4401. Limited by oxidation to 815°C. If product contamination by scale particles is a consideration, consider a 650°C limitation.
- 321 stainless, 1.4541, has about a 50-60°C advantage over 304, and is used to 870°C.
- 316Ti, 1.4571, used to 900°C in Europe. This grade is not available in North America.
- 309S, 1.4833, is useful to about 1010-1040°C, above which oxidation performance becomes unsatisfactory.
- 800H, 1.4876, is somewhat more oxidation resistant, with a practical limit of about 1095°C.
- 310, 1.4545 is reasonably oxidation resistant to about 1150°C, although the strength is quite low at this temperature.

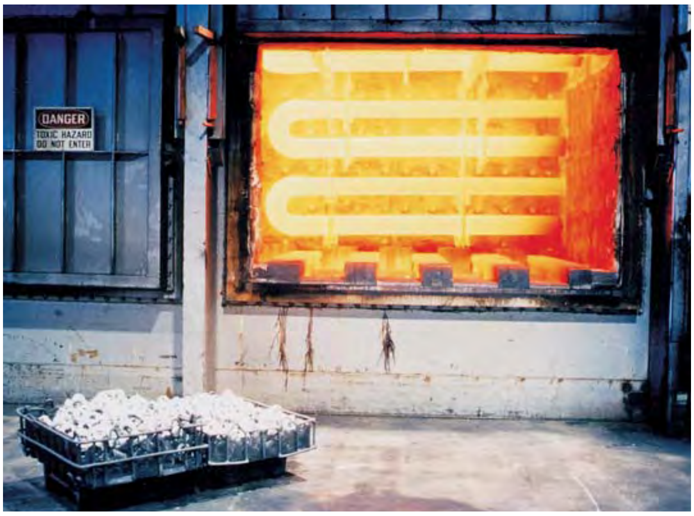

Fig. 1: Radiant U-tubes mounted horizontally in a heat treat furnace

- 314, 1.4841, tolerates higher temperatures than does 310, with good carburization resistance. In North America this grade has been replaced by RA330, 1.4886.
- RA 253 MA®, 1.4893, has superior oxidation resistance to a limit of 1095°C. Above this temperature the oxidation resistance may be adequate, but not exceptional.

Typical operating temperature of radiant U-tubes are 980°C. Exothermic atmosphere used for annealing. Tubes were fabricated with a 150 mm OD x 3 mm wall firing leg and a 130mm OD x 3mm wall exhaust leg. **Fig. 1** shows it after 10 months in service.

RA330® (EN 1.4886) combines useful oxidation resistance and fairly high melting point to survive extreme temperature abuse. Muffles of RA330 are used at 1150-1180°C.

RA 353 MA®, EN 1.4854, has a melting point similar to that of RA330, with better oxidation resistance in laboratory tests. Field experience with muffles, calciners, vortex finders and cement kiln burner pipes show it to tolerate extreme temperature better than does RA330. It is considerably stronger than 601, 24851, at high temperature.

The RA 353 MA retort in **Fig. 2** is used for diffused aluminide coating of turbine blades. Process temperature is 915 to 1070°C, depending upon the blade to be coated. As the retort is externally fired, the retort wall may be expected to operate 50-60°C above process temperature.

RA333®, 2.4608, resists both oxidation and carburization. 1200°C may be considered a practical upper limit. Stagnant conditions at this temperature might not be desirable.

Fig. 2: RA353 Chromalloy - NV after 2 years

Fig. 3:
Broken radiant tube

The RA333 radiant tube in **Fig. 3** lasted 8-1/2 years before failure from local overheating. Nine other tubes remained in service in this three-row continuous pusher carburizer furnace. 625, 2.4856, is limited by oxidation resistance to 980°C in service. 601, 2.4851, very oxidation resistant through 1200°C. Deforms somewhat more than does RA333 and RA 353 MA in extreme temperature applications.

Oxidation

Chromium is the one element present in all heat resistant alloys, the protective chromia scale being the basis for high temperature environmental resistance. Silicon and nickel are next in importance, then aluminum and rare earths.

Oxidation rates are influenced by thermal cycling and creep which increase scale spalling. Contaminants such as alkali metal salts may damage the chromia scale. The particular atmosphere involved is important. Water vapor in the atmosphere increases oxidation rates of high iron alloys more than of high nickel grades.

Carburization

Chromium, nickel and silicon are three major elements which confer resistance to absorbtion of carbon. Nickel and silicon lower the maximum solubility of carbon and nitrogen. Carburization is normally an issue because highly carburized alloys become brittle. Above about 1 % carbon, most wrought heat resistant alloys have no measurable room temperature ductility. Carburization may occur in hydrogen or nitrogen atmospheres if they pick up carbon from residual oil on the work load.

Metal dusting, also known as catastrophic carburization or carbon rot

This is a metal wastage, not embrittlement, phenomenon. It can occur in any heat treating furnace with a carburizing atmosphere. The phenomenon attacks metal components where they pass through the furnace walls. Here the atmosphere is stagnant, with temperature about 600°C. In the steel heat treating industry, some four decades of experience have shown that wrought RA333 and the cast grade Supertherm® are two of the best choices. RA330 is not particularly resistant to metal dusting, and 800 H is markedly worse. The high nickel 600 alloy retains ductility, but is the least desirable to resist metal dusting in a carburizing furnace. Appropriate alloy selection for steam-methane reformers is still a subject for discussion. 310 stainless has been used in petrochemical metal dusting environments.

The example in **Fig. 4** is from a rotary retort used to carburize small parts at an operating temperature of about 940°C. Spiral flights of 5 mm RA310 welded to the inside served to transport work pieces through the retort. As the retort was externally fired, the 8 mm 600 alloy shell was above the temperature range for metal dusting. Metal dusting was a serious problem with flights at the entry end of the retort. Here the cold work pieces chilled the RA310 flights down into the metal dusting temperature range.

Sulfidation

High chromium, low or moderate nickel minimizes sulfidation attack at high temperature. Generally, alloys with more than 20 % nickel are unsatisfactory.

Strength

Creep-rupture properties at temperature are usually available from the various producers, and many alloys are covered by the ASME Boiler and Pressure Vessel Code.

Fig. 4: Part from a rotary retort used to carburize small parts at an operating temperature of about 940°C

Thermal stability

After long exposure to the 590 - 870°C temperature range, many of the higher chromium alloys precipitate a brittle intermetallic compound known as sigma phase. Molybdenum contributes to this phase. Sigma reduces room temperature impact strength and ductility. The quantity and morphology of the sigma phase determines severity of embrittlement. Usually the metal is brittle only near room temperature, and retains reasonable ductility at operating temperatures above perhaps 315 - 540°C. Higher nickel grades such as N08811, N08330, N06600 or N06601 are not susceptible to embrittlement by sigma. The cast heat resistant alloys, being so much higher in carbon, loose ductility due to heavy carbide precipitation in service.

Fabricability

Fabricability is not usually a significant issue with conventionally melted wrought alloys. Oxide dispersion strengthened grades such as MA956® or Kanthal® APM offer unmatched strength and oxidation resistance at extreme temperature but are extremely difficult to form and join by conventional means.

Temperature of Operation

This will be different than the process temperature. Copper brazing, for example, may be carried out at 1120°C. However the muffle wall is hotter typically 1180°C. Reported temperatures are normally process temperatures.

Design

Allowable stresses are often based on ASME design allowable. Much thermal processing equipment uses for design stress either one half of the 10,000 hour rupture strength, or one half of the stress to cause a minimum creep rate of 1% in 10,000 hours. Above about 540°C, creep or rupture is the basis for setting design stresses. Materials are no longer elastic, but deform slowly with time. Where possible pinned joints are preferable to rigid weldments in order to permit differential expansion of the components. Likewise corrugations permit the alloy to flex somewhat, rather than crack in thermal cycling conditions.

Fig. 5: Serpentine tray of 6 and 9.5 mm RA 330

Fig. 5 shows serpentine tray of 6 and 9.5 mm (1/4' and 3/8") RA330. The tie bars are welded on one side only, with generous room for expansion and contraction at the other. A combination of "serpentine" flat bars and loose pinned joints permits this design to survive many hundreds of oil quench cycles from 870-980°C.

Weldments

Incompletely penetrated weld joints are the most common cause of weldment failure in high temperature service. Full penetration welds are imperative. In thermal or mechanical cycling, an unwelded area behaves as a large crack or notch. Repeated thermal strains cause the "crack" to grow outward through the weld bead, a small step each cycle. Since this crack cannot be seen from the outside, there is no warning sign that the part is about to break (**Fig. 6a and b**).

Thermal expansion

A major cause of distortion and cracking in high temperature equipment is failure to adequately address the issue of thermal expansion, and differential thermal expansion. A temperature gradient of as little as 110°C is sufficient to strain metals beyond the yield point.

Molten netals

The molten metals most likely to cause an industrial problem are copper and silver braze alloys, zinc and aluminum. As a very rough rule of thumb, low melting metals attack the high nickel alloys more than lower nickel or ferritic grades.

Cast heat resistant alloys

Heat resistant alloy castings are available in chemistries similar, though never identical, to those of the wrought alloys. Selection of wrought vs cast versus will depend upon experience, economics, and delivery time.

Advantages of cast alloy

- Initial Cost. Since cast parts avoid all the forging, rolling, cutting and welding of a fabrication, the price per pound of fixture may be lower.

Fig. 6a: This fully welded joint can resist both thermal and mechanical fatigue

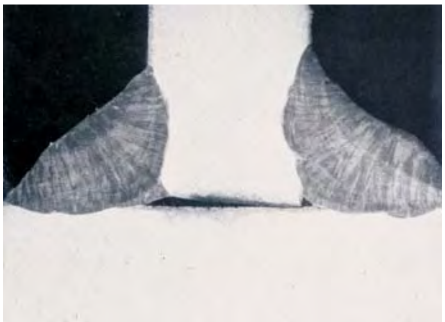

Fig. 6b: The unfused void in this fillet weld acts as a stress riser and may cause premature failure

- Creep Strength. Similar compositions are inherently stronger at high temperature in the cast form than in wrought. This is because of the microstructure, and because cast heat resistant alloys are usually much higher carbon than the wrought "equivalent".
- Shapes. Certain shapes can be cast that are not commonly available hot rolled, or that cannot be fabricated economically from available wrought product forms.
- Compositions. Some alloys are available only as castings, because they lack sufficient ductility to be worked into wrought forms. This is particularly true of the very high chromium alloys.

Disadvantages of cast alloy

- Weight. Cast parts are almost invariably thicker and heavier than the equivalent fabrication. This increases the dead weight that goes through each heat treat cycle. There is no profit in heat treating the furnace fixture. With radiant tubes and muffles thicker cast walls increase fuel costs for the same volume of work load.
- Ductility. Most cast alloys quickly become very brittle in service. They are unable to withstand rough hand-

ling when cold, and weld repair can be difficult.

- Soundness. Castings invariably have some degree of porosity, internal shrinkage cavities, oxides and cold shuts. When these defects are open to the surface they are subject to attack by carbon deposits or molten salts.
- Pattern cost. A pattern must be made for each different part design. This is all right for production runs, but quite uneconomical for one-off fixtures.

Advantages of wrought alloy

- Section Size. Wrought alloys are available right down to foil thickness. Thinner sections often permit weight reduction of 50 % or more. With lighter sections the initial cost of a fabrication becomes competitive with, or less than, a casting. Handling the fixture is easier, and much less unproductive metal goes through each furnace cycle.
- Thermal Fatigue. Thinner sections that reduce thermal stresses, and the inherently greater ductility of wrought metal, promote better resistance to thermal cycling and shock.
- Surface finish. The smooth surface of wrought alloy helps avoid focal points for accelerated corrosion by molten salts or carbon deposits. **Fig. 7** illustrates the effect of cast alloy surface and internal defects versus wrought alloy soundness, on service performance. This grid suspended loads in a gantry furnace at a commercial heat treat shop. The work was neutral hardening from temperatures up to 1010°C, quenched in either molten salt, oil or brine. When the cast HT (35% Ni 17%Cr) grid was practically new and had been exposed to only a few cycles, a particular job required increased working area for the grid. To do this, sections of RA330 alloy flat bar were was formed and welded to the outside of the existing cast grid. As can be seen in Fig. 7 the cast alloy portion suffered surface attack from soot and the quenching salt, and failed from thermal fatigue. Note the cracks in the center of the cast ribs. These occur along the plane of weakness of the dendritic structure. The wrought alloy RA330 exhibited very little surface attack and no fractures.

Fig. 7: Effect of cast alloy surface and internal defects versus wrought alloy soundness

- Soundness. As above, wrought materials are normally free of the internal and external defects such as shrink, porosity, etc., found in castings.
- Availability. Wrought heat resisting alloys are immediately available from stock in numerous product forms. Fabrications are quickly procured to minimize expensive down time.

Disadvantages of wrought alloy

- Creep strength. Few wrought alloys match the high strength of heat resistant castings. Where creep-rupture is truly important, this must be considered in product design (although, RA 353 MA is close).
- Composition. Grades such as 50Cr 50Ni, 28Cr 10Ni or 35Cr 46Ni have excellent high temperature properties but are too brittle to hot work. These alloys are available only as castings.