Oxidation

For our purposes, this means the high temperature chemical reaction of a metal with the oxygen in the air. Simply put, most metals can burn when they get hot enough. Some, like magnesium (once used in flash bulbs) and titanium do burn in the conventional sense and may cause a serious industrial fire. Even iron burns. Of course, lighting a match to a nail does absolutely nothing. But if one takes very fine iron wire—specifically, 0000 steel wool—it may indeed be ignited by a match. There is no actual flame, but a red hot "coal" develops and enough sparks fly to endanger clothing.

There are two basic ways in which a metal may be resistant to oxidation. First, it may be inert and simply not react chemically with oxygen in the air. Two examples come to mind, the precious metals gold (Au) and platinum (Pt). Because of its high melting point, 3217°F (1769°C), coupled with oxidation resistance, platinum is actually used for some laboratory ware and other items that must withstand extreme temperature.

The second way a metal may resist oxidation, and the one of interest to us, is that the metal or alloy may form an adherent oxide film, which protects it from further oxidation. The element most often used to form such a protective oxide layer, or scale, is chromium. It forms the oxide Cr_2O_3, also known as chromia.

Although chromium itself oxidizes even more readily than iron, the oxide it forms is very thin, and adheres tightly to the metal. This oxide layer forms very quickly at high temperature, but once formed it protects the metal against further oxidation. The chromia scale also protects the alloy against carburization and sulfidation, to a degree. The protection is by no means perfect. The scale contains defects through which oxygen and other elements may pass, to continue to react with the alloy. Scale also cracks from both thermal and mechanical strains, and small pieces spall off each time the metal is cooled down. For a high temperature alloy to have useful oxidation resistance, the scale must be able to "heal" these defects, by more chromium diffusing to the surface to form a new protective film.

Other elements are added to the alloy to improve the protective nature of this oxide film or scale. One of the most effective is silicon. Silicon oxidizes to SiO_2, or silica. If enough silicon is present, the silica forms a sub-scale underneath the chromium oxide scale. This silica subscale is how silicon provides resistance to carburization, in alloys such as RA330. At the 1.2% Si level in RA330, silicon also contributes to oxidation resistance. In RA85H, which is no longer produced, the silicon was much higher, 3.5%. At this high level silicon appeared to offer resistance to molten alkali salt corrosion.

The effectiveness of the chromium oxide scale may be improved by very small additions of rare earth elements, such as cerium. Cerium promotes a thinner scale, which is more protective against oxidation because it cracks and spalls off less than would a thicker scale. It is the 0.04% cerium in RA 253 MA that is largely responsible for the excellent oxidation resistance of this rather lean 21Cr, 11Ni alloy.

Aluminum is also used to improve oxidation resistance. In order to actually develop an Al_2O_3, or alumina, scale a rather high amount of aluminum is required. At 2.2% aluminum, RA 602 CA alloy will form an alumina subscale. This contributes to the oxidation resistance of RA 602 CA. RA 602 CA does not oxidize internally. The 1.4% Al typical in alloy 601 is not enough to form an alumina scale, but it is enough to enhance oxidation resistance of 601. Because of aluminum at this somewhat lower level, 601 oxidizes internally. This is not a problem in plate gauges, though perhaps it may be a consideration in thin sheet. The 4.5% aluminum in Haynes alloy 214 is enough to form an actual alumina scale. and 214 is extremely oxidation resistant above 1800°F/982°C.

The Protective Film

While chromium is given credit for promoting oxidation resistance and is without question the most effective element in this respect, it is actually the most easily oxidized. This may sound like double talk, but it really isn't. When pure chromium or a chromium-bearing alloy is exposed to oxygen, even at room temperature, it is oxidized and a layer of chromium oxide (and oxides of other elements as well) is formed. Even the chromium plate on automobiles, or the cutlery on our dinner tables, has a microscopically thin and transparent film of chromium oxide present.

When formed at high temperatures, the oxide coating becomes green, black, blue or yellow, depending upon its thickness and which of the numerous chromium oxide compounds is formed. This in turn depends upon the temperature and availability of oxygen to combine with chromium. The oxide layer is dense, is inclined to be tightly adhering, and effectively seals out the air or oxygen from the metal underneath. So long as the oxide layer is intact, the metal is protected and further oxidation proceeds very slowly.

Several things may tend to destroy our protective layer:

Expansion and contraction, as the result of heating and cooling, will "pop" the oxide layer, because the base metal and the oxide expand and contract at different rates. The more rapid the rate of expanding and contracting, or the more quickly the metal is heated and cooled, the more hazard there is of the protective coating flaking off.

Certain combinations of chromium, iron, nickel, silicon and other oxides are more tightly adhering than others at different temperatures. With some alloys it is possible to reach a temperature where the scale or oxide is no longer tightly adhering and will be loose, thereby offering little or no protection. Thus, an excessive temperature for the specific alloy can destroy the protection normally offered by the oxide layer. Some examples are 321, which is acceptable at 1600°F (870°C) but scales unacceptably at 1800°F (980°C), and 309, which isn't very useful above 1900°F (1040°C).

Composite radiant tube, RA333 for 4 feet (1.2metre) on the firing end, middle portion RA330 and exhaust end fabricated of RA309. Used at a nominal furnace operating temperature 1750°F (955°C) for annealing malleable iron castings. It is to be expected that the tube metal temperature would be perhaps 100—150°F (55—85°C) higher. A jam-up in the furnace broke the tube. Note the crater-like appearance of local oxidation or “warts” the RA309.

When an alloy is used at a temperature exceeding its capabilities the scale may break down locally, a condition sometimes called “warts”, or “nodules”. We have observed this on 309 (above) and 310, occasionally on RA 253 MA, RA330 and 600 alloy. On one occasion we saw warts on an RA333 brazing muffle. Upon investigation we found that the RA333 had been heated in service to the incipient melting temperature, perhaps somewhere above 2370°F. The grains were sliding apart so as to leave voids at the triple points, resulting in apparent porosity of the 11gage (3mm) muffle wall.

Mechanical deformation and creep, such as the stretch of a bar under load, may also destroy the protection. While the metal is ductile and yields in creep, the oxide coating is fragile and brittle and will spall off. In service, a given item may appear to have insufficient oxidation resistance, whereas that particular property would have been more than adequate had the strength been sufficient to avoid excessive creep. Laboratory data which do not duplicate cyclic conditions or stresses imposed in actual service can be misleading as a measurement of an alloy’s oxidation resistance.

Of great concern are environments that promote the destruction of the protective layer by some chemical reaction. For example, we know of one case where minute amounts of potassium nitrate/nitrite austempering salts were present on fixturing used in a carburizing atmosphere. The salts attacked the protective oxide coating, so that a normally carburization resistant alloy carburized very quickly and uniformly.

In years past, we knew of a few cases where parts being heat-treated were first coated with sal ammoniac (ammonium chloride). The presence of this chloride salt resulted in a chemical attack upon the protective oxide coating of the furnace fixtures. Alloys normally selected for the strength, oxidation resistance and thermal shock resistance requirements were not suitable.

Another form of chemical destruction that may be encountered is corrosion from welding fluxes. Fluoride-bearing fluxes from coated welding electrodes must be carefully and thoroughly removed. Otherwise they continue to function as a flux, damaging not only oxidation resistance, but also carburization resistance.

Green rot might be considered one form of destruction of the protective oxide coating. To the best of our knowledge, green rot tends to be more prevalent in alloys containing about 65% or more nickel. Green rot is the result of the alloy being alternately exposed to oxidizing and reducing conditions.

When the alloy is exposed to the oxidizing environment, a protective oxide coating is formed, as we previously discussed. When the alloy is exposed to highly reducing conditions, the nickel and other less stable oxides may be reduced to pure metal, which disappears as a powder; but the chromium oxide, being more stable, is not reduced. Upon exposure of the alloy to an oxidizing environment once more, the oxygen is free to penetrate to the metal and form another layer of oxide, since there are now voids in the coating where some of the oxides previously existed.

With continuous exposure to the two conditions, a mass is eventually formed consisting only of porous chromium oxide, with or without other oxides that may have been sufficiently stable to resist reducing. This actually has little strength and no ductility. It has the characteristic greenish-black color of chromium oxide and, upon fracture, has the appearance of rotten wood. Hence the name, green rot.

Catastrophic Oxidation

Catastrophic oxidation is, as its name implies, oxidation that proceeds so rapidly that complete failure of the material occurs in an extremely short time. Certain elements, such as molybdenum, columbium (niobium), vanadium, and tungsten, form oxides that are volatile at relatively low temperatures. If these oxides are formed and retained in the scale, they act as fluxes and destroy the protective film[1, 2, 3].

This 316 stainless (S31600) bar was originally 3/4” (19mm) dia. It operated at 1800°F (982°C) as an electrical heating element. Sections that were covered with ceramic insulation suffered catastrophic oxidation from the 2%Mo in 316, and reduced in section to less than 1/4” (6mm) diameter.

The typical chemistry of 316 is 16.4Cr 10.2Ni 2.1Mo. Generally 1500°F (816°C) is considered the maximum long-time use temperature of 316 even in a free-flowing atmosphere

The effect of molybdenum is important enough that we would like to quote directly from the late Howard S. Avery's classic work on heat resistant alloys, Cast Heat-Resistant Alloys for High-Temperature Weldments: "Where in fact the addition of molybdenum has conferred better hot strength, the chief problem may be surface stability, especially in the 1800—2300°F (980—1260°C) range. This is most serious under those conditions that cause catastrophic oxidation which stems from the volatile nature of molybdenum oxide (MoO_3). This oxide is likely to form in stagnant atmospheres, with a threshold for trouble around 1400—1500°F (760—816°C)."

Catastrophic oxidation, continued

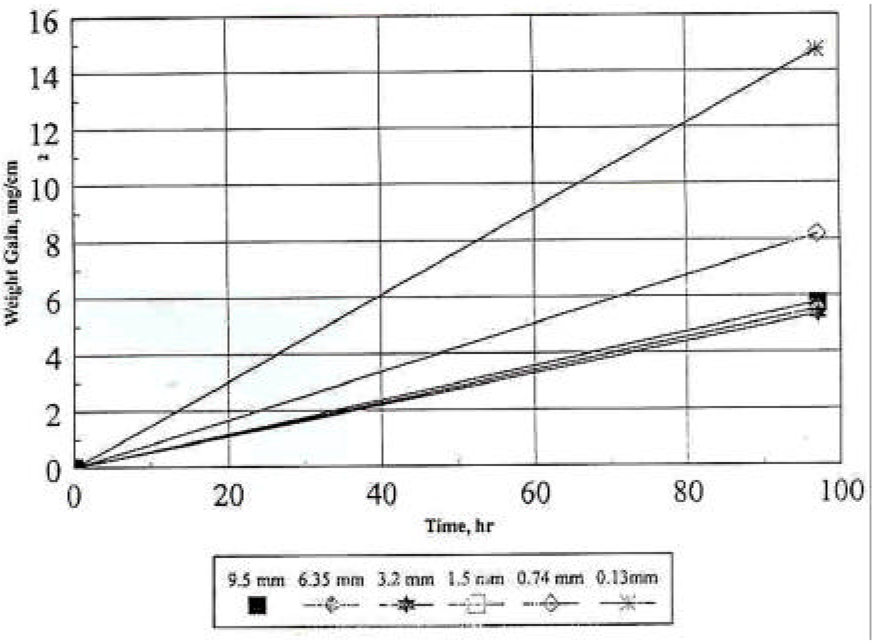
Catastrophic oxidation may be a serious problem under certain operating conditions. That is, a stagnant atmosphere, or solid deposits under which the atmosphere is of course stagnant, and extreme temperatures. Alloy X (N06002, W.Nr. 2.4665), containing 47% nickel, 22% chromium and 9% molybdenum, may completely disappear from catastrophic oxidation when heated for some months at 2200°F (1200°F). At lower temperatures in free-flowing atmospheres alloy X is highly oxidation resistant. It has, after all, served for decades as the primary alloy used in gas turbine flight engine combustors. However, alloy X may not well tolerate stagnant conditions or temperature extremes.

Alloy X (N06002) bar exposed to a metal dusting environment. To keep the temperature near 1100°F (~600°C), where metal dusting is most likely to occur, the rod was packed in fibrous insulation. Because the atmosphere under the insulation was stagnant, in our opinion the attack shown here is more likely representative of catastrophic oxidation, rather than metal dusting.

Metal Thickness

Thin things burn faster than thick. Thin sections have a lesser total amount of chromium available to reform the protective scale. Most of our data and experience is with plate gauges, roughly 3/16—1/2" (~5—13mm). The normal concern is that the plate not lose enough thickness that it is no longer structurally sound. One should be cautious about applying this experience to thin sheet. For example, a metal loss of about 0.020" (1/2mm) per side may not seriously impede the operation of a plate item 1/2" (12.7mm) thick. But that same loss on 16 gage (1.6mm) sheet would quite destroy its usefulness.

Metal Thickness, continued

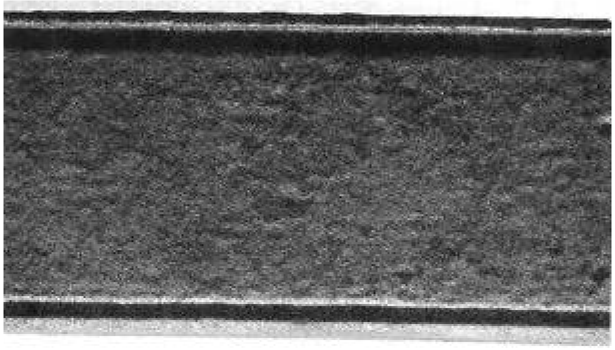


Isothermal oxidation at 2100F (1149C) for 97 hours, versus thickness of RA330.
Test coupon thickness: sheet 0.005, 0.060, 0.120, plate 1/4, and 3/8".

Grain Size

As the protective oxide layer flakes away or is otherwise damaged, diffusion of chromium to the surface continually reforms, or "heals", the scale. The diffusion rate of chromium is orders of magnitude greater along grain boundaries than it is through the grain itself. Fine grain size improves the ability of the scale to re-form and to heal damage[4].

We observed the effect of grain size on oxidation of S30400 stainless flat bar after long time service.

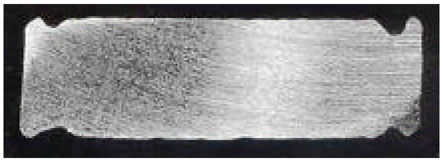


Type 304 stainless "belly band", cross section 11.5 x 38 mm.

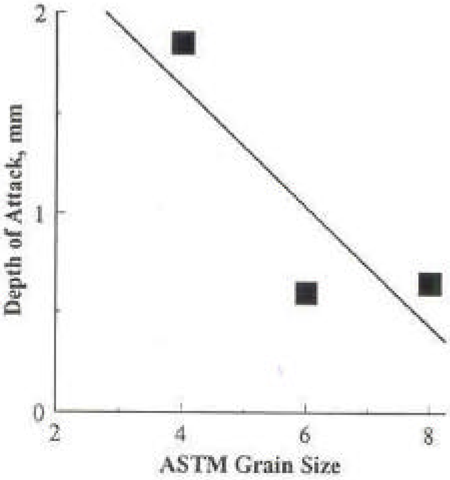
This band was used to reinforce corrugated RA309 inner covers used for batch annealing carbon steel coils.

Grain Size, continued

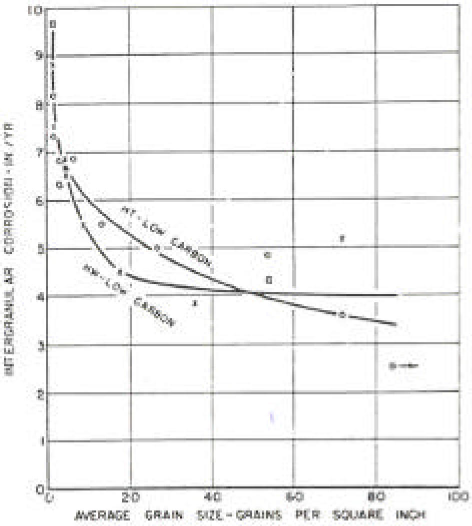
In service this band was exposed to products of combustion of natural gas with excess air at about 1600°F (870°C) for perhaps five years. The flat bar for this band was produced by shearing strips from 1/2” (12.7mm) plate. The shearing operation heavily cold worked the edges.



Metal loss due to oxidation was 0.6mm per side over most of the band. There was a narrow zone of deep attack parallel to and about 2,5-3mm from each sheared edge.



The bulk of the metal had grain size ASTM 7. The heavily cold worked sheared surfaces recrystallized in service to grains as fine as ASTM 8. A short distance back from the edge, coincident with the heavily oxidized zone, the grain size was as coarse as ASTM 4. This is the zone which was cold worked in the critical range for grain growth. The relation between metal wastage and grain size of this 18-8 stainless is shown at left.



The effect of grain size on hot salt corrosion is similar. An Alloy Casting Institute study[5] of the grain size effect on intergranular corrosion rates of low carbon cast Ni-Cr-Fe alloys in molten chloride salts is in agreement. The ACI exposed samples for 50 hours at 1600°F (871C) in a neutral salt bath containing 55% $BaCl_2$, 25%KCl & 20% NaCl. The reduction in attack of HW (12%Cr 60%Ni) and HT (15%Cr 35%Ni) with decreasing grain size is shown at left.

Laboratory Oxidation Testing

In order to evaluate new and competitive alloys we perform considerable laboratory oxidation testing at Rolled Alloys, at temperatures up to 2250°F (1232°C)[6, 7] . We measure weight gain, that is, the total amount of oxygen (and nitrogen) that has reacted with the test specimens. Specimens are usually of plate gages, and the tests are cyclic. Samples are heated in porcelain crucibles, 4 to 6 in a tray, for about 160 hours (one week) at temperature. The tray is then removed from the furnace, lids are quickly placed on the crucibles to contain spalling oxide, and the assembly allowed to air cool to room temperature. The entire crucible, containing specimen and scale, is then weighed every cycle. Results are reported as weight gain, in milligram/centimeter^2 .

The numerical results are valid only for the specific conditions of the test. Which means they are not useful for predicting metal wastage of components in actual service. However they are of value when one compares the data from new alloys, with those of existing grades. For example, we have a great deal of experience with the good performance of RA333 and RA330. Likewise, 309 is about the only one of our heat resistant alloys that occasionally gives disappointing performance, generally around 1900°F (1040°C) or above.

If an alloy performs well on test, we feel that means it MAY perform well in service. A simple coupon test does not simulate all the things that can happen in service. So, it is possible for an alloy to look very good in the laboratory and not at all so good in production equipment.

While we like to think our tests provide useful guidance, there are a number of conditions, common in high temperature equipment use, which are not well simulated by laboratory oxidation testing:

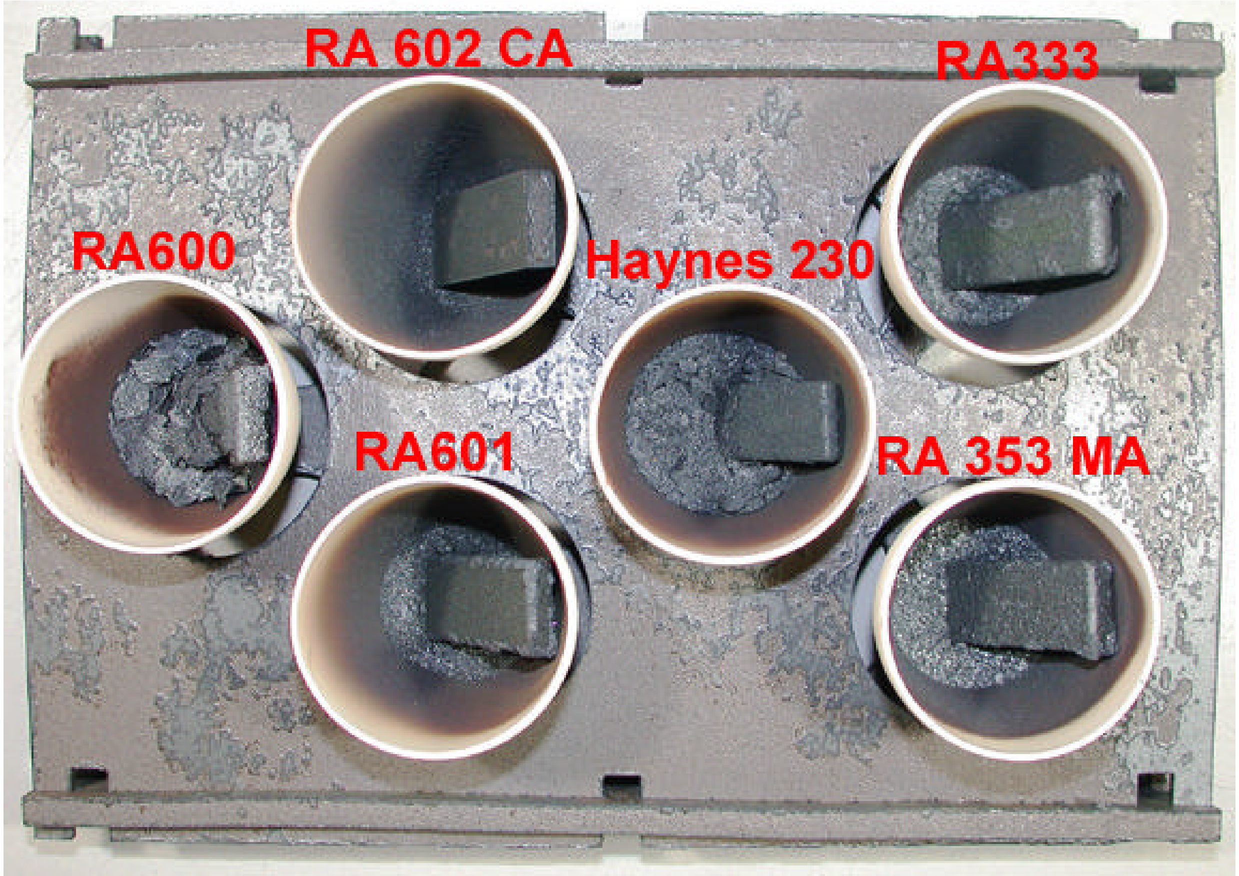
1. Thermal Cycling. This is more or less addressed by cycling the specimen to room temperature weekly. More rapid cycling means more scale spalls off, increasing oxidation rates, more so for some alloys than others. For example, in static 1000 hour oxidation testing 310 is somewhat superior to RA330. When thermal cycling is added, RA330 better retains its protective oxide.

2. Creep Strain. This is not at all addressed in the lab. Creep strain, as well as thermal cycling, increases the amount of scale which spalls off the coupon.

3. Stagnant Atmospheres. There is little or no flow of atmosphere in certain areas of electrically heated equipment, and underneath insulation or solid deposits. Alloys with high molybdenum contents are subject to catastrophic oxidation under these conditions, though they may perform rather well in our open air test.

4. Atmospheres other than dry air. The H_2O content of the atmosphere affects oxidation rates. High water content increases the metal wastage of low nickel alloys faster than it does the higher nickel grades

Laboratory Oxidation Testing, continued



Oxidation test after 2880 hours at 2200°F (1200°C)

And, finally, the laboratory test does not properly simulate time. 3000 hours seems a reasonable length of time to run a test in our laboratory, but that is still only about 4 months. If one expects the equipment to last 1, 2 or 10 years, it would be hard to make a case that a 4 month test adequately represents service conditions. The specimen continually changes chemistry throughout the test (it loses chromium, silicon and aluminum by scaling). Thin samples, simply from having less total chromium, may show greater oxidation rates than thick specimens. In our considered view, significant extrapolations of oxidation, or other high temperature corrosion data, are not valid. The declining availability of experienced engineers in the U.S.A. has generated pressure to extrapolate such data, valid or not.

Data shown on the following bar graphs is all for 3000 hour (~18 weeks) exposure, in order to compare all alloys for about the same exposure time. All but the RA309 tests were run for 3000 hours, that one being extrapolated from a 1600 hour run. As this is weight gain data, high numbers mean heavy oxidation, small numbers a relatively light degree of oxidation.

One would expect to use these numbers, along with service experience, as a guide to an alloy's usefulness. We emphasize that, unlike what is assumed about aqueous corrosion data, oxidation data ought in our opinion be viewed qualitatively.

Laboratory Oxidation Testing, continued

Numbers under 20 may give assurance that the alloy, in plate form, should not lose structural integrity due to metal loss. One might want a little actual service background when considering alloys with weight gains in the 100-300 mg/cm^2 range. One example is 304 stainless, which gains 64 mg/cm^2 at 1600°F (871°C), and in the neighborhood of 300 mg/cm^2 at 1800°F (982°C). By experience, we know that 304 1/4" plate will simply disappear in 2-3 months when used in air around 1700-1800°F (930—980°C). We would look at the higher alloys, for more elevated temperatures, somewhat differently. Note 600 alloy which shows a 153 mg/cm^2 weight gain at 2100°F (1149°C). Nevertheless, alloy 600 plate is a useful material for retorts and muffles operating in the 2100-2200°F (1150—1200°C) temperature range. Likewise RA 353 MA is used quite successfully at such temperatures. RA 602 CA is clearly the best by far in our test series. The good resistance to scaling of RA 602 CA in test has also been borne out by service experience in rotary calciners, CVD retorts, and at least one AOD charge chute..

One should also bear in mind that these data still represent simple laboratory oxidation testing, which does not take into account many of the ways by which the protective oxide scale may be damaged. The alloys were cycled to room temperature once a week. More rapid thermal cycling would not only increase oxidation rates but might also change the relative performance of some alloys. In static 1000 hour oxidation testing, for example, 310 is somewhat superior to RA330. When thermal cycling is added, RA330 better retains its protective oxide. Another point to remember is that alloys high in molybdenum and columbium may be sensitive to catastrophic oxidation, particularly under stagnant atmospheres.

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