

Understanding Conditions that Affect Performance of Heat Resisting Alloys

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Chemistry and Temperature Gradients

The heat resistant alloys of concern in this article are the wrought, solid solution strengthened nickel-chromium-iron alloys used as structural elements or fixturing in the thermal processing industries. These alloys are intended to survive service temperatures which may range from below 1400 to 2300°F, atmospheres from vacuum to carburizing, thermal cycling from slow furnace cool to repeated brine quench and corrosive environments ranging from air to hot salt fumes or low-melting-temperature metals.

Failures are most commonly due to thermal fatigue, a situation which has been recognized in the published literature at least back to the 1930's¹ and which has probably existed for as long as heat resisting alloys have been used (since the late 'teens or early twenties). Excessive creep deformation and embrittlement from carburization or phase changes are also common failure modes. Less common but highly aggravating to the user are failures due to hot corrosives such as neutral salt fumes and various low-melting-temperature metals. High temperature rupture failures do not occur often, and when they do are usually the result of inadvertent overload or over temperature. Occasionally melting occurs, particularly if severe carburization has lowered the melting point of the alloy.

Alloys used to resist these conditions may be composed of from 15 to 25% chromium, and zero to 76% nickel with the balance mostly iron. Some of the more commonly used materials are listed in Table I. Strength, oxidation and carburization properties are modified by additions of carbon, molybdenum, cobalt, tungsten, silicon, columbium, aluminum or titanium.

Table 1 Nominal Compositions of Wrought Heat Resistant Alloys

Alloy	C	Mn	Si	Cr	Ni	Mo	Co	W	Ti	Al
RA 333	.05	1.5	1.25	25	45	3	3	3	-	-
RA 330	.05	1.5	1.25	19	35	-	-	-	-	-
RA 330HC	.40	1.5	1.25	19	35	-	-	-	-	-
RA 446	.10	1.0	0.5	25	-	-	-	-	-	-
RA 85H	.20	0.8	3.5	18.5	14.5	-	-	-	-	1.0
309	.05	1.5	0.8	23	14	-	-	-	-	-
310	.05	1.5	0.5	25	20	-	-	-	-	-
800	.05	0.75	0.5	21	32	-	-	-	0.4	0.4
600	.08	0.5	0.2	15	76	-	-	-	-	-

The functions of these various elements generally are to prevent the alloy from losing excessive section thickness through oxidation, to permit the alloy to retain useful strength at elevated temperature and to enable the alloy to resist one or more hot corrosive environments.

Function of Specific Elements

Some understanding of each element's function can

assist in evaluating the various alloys which might be considered for a job.

Chromium is the basis for high temperature oxidation resistance, hot corrosion resistance and, to some extent, carburization resistance. Chromium itself is a very active and readily oxidized element which forms a tight oxide scale (Cr_2O_3) on the alloy. So long as this scale layer remains intact it greatly reduces the rate at which the base metal is further attacked by oxygen or other elements.

In nickel-chromium-iron alloys high chromium contents may promote formation of the brittle intermetallic phase sigma upon long exposure to the 1100-1600°F temperature range. This tendency may be counteracted by sufficiently high levels of nickel and/or cobalt.

Chromium is a ferritizer and the 25-26% chromium-iron alloys form little or no austenite right up to the melting point.

Nickel is required to stabilize the austenitic structure, with respect to transformation to ferrite or martensite, and with respect to sigma formation. Nickel also improves oxidation resistance partly by reducing oxide spalling under thermal cycling conditions. Nickel confers resistance to carburization by reducing matrix solubility for carbon and by the fact that nickel itself does not form a stable carbide. High nickel contents increase carbon diffusion rate. Nickel combines readily with sulfur to form low-melting-temperature compounds. As a general rule, high nickel alloys are much more susceptible to sulfidation attack than are the lower nickel alloys.

Iron is a mild strengthening agent, to the extent that it replaces nickel. However, iron is readily oxidized, and the iron content must be protected from oxidation by the chromium in the alloy.

Silicon is added in amounts of about 1 to 2% to increase carburization resistance. Silicon appears to improve resistance to carburization primarily through its effects on the oxide scale, and secondarily by decreasing matrix solubility (increasing thermodynamic activity) for carbon. In lower nickel alloys such as 310, high silicon promotes sigma formation.

Tungsten is a good solid solution strengthening agent with few or no metallurgical drawbacks in existing alloys.

Cobalt is a mild strengthening agent which improves oxidation resistance by reducing the tendency for localized oxidation attack of the form described variously as oxide nodules or "warts".

Molybdenum is a solid solution strengthening element used in commercial heat resisting alloys in amounts up to 9%. Molybdenum bearing alloys may be susceptible to catastrophic oxidation under stagnant atmospheres or temperatures above about 2000°F². The MoO_3 , which forms, if not removed by free-flowing atmosphere, will aggressively remove the protective oxide scale. How much

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molybdenum may be tolerated in an alloy depends upon the chromium and nickel levels and, of course, the particular service environments.

Columbium is added as a potent solid solution strengthener and also improves effectiveness of carbide strengthening. Minor additions ($\frac{1}{2}\%$) decrease, and larger additions (2%) improve, weldability of fully austenitic materials. A disadvantage of columbium additions is a marked reduction in oxidation resistance³ observable at high service temperatures.

Titanium is added up to about 1% to improve carbide strengthening. Titanium enters the oxide scale and may affect oxidation resistance, presumably favorably. Titanium is a sigma former and in higher amounts may form gamma prime with nickel.

Aluminum is used as a deoxidizer in melt practice. It is deliberately added to some heat resistant alloys up to 1.7% to promote better adhesion of the oxide scale. Aluminum is a sigma former, and sufficient amounts form gamma prime with nickel.

Manganese is added to heat resisting alloys solely to improve hot workability. In some fully austenitic weld fillers, such as RA-330-04, significant manganese additions are made to improve weldability.

Carbon acts as a strengthening agent through formation of chromium or other alloy carbides. Most wrought alloys contain about 0.04-0.10% carbon, although a few special purpose alloys contain as much as 0.40% carbon. Carbon in solution is a powerful austenitizer.

Microstructure Related to Properties

In addition to chemistry, the properties of any metal are related to microstructure. Fig. 1 illustrates an example of annealed RA-330, with a few scattered carbides in a matrix of about ASTM 5 grain size. Numerous annealing twins are present. This microstructure, with the exception of grain size, is typical of a wide range of alloys from common stainless up through the nickel alloys. RA-333, a higher alloy material, exhibits a larger volume of dispersed carbides, as illustrated in Fig. 2. The grain size of this sample is also about ASTM 5.

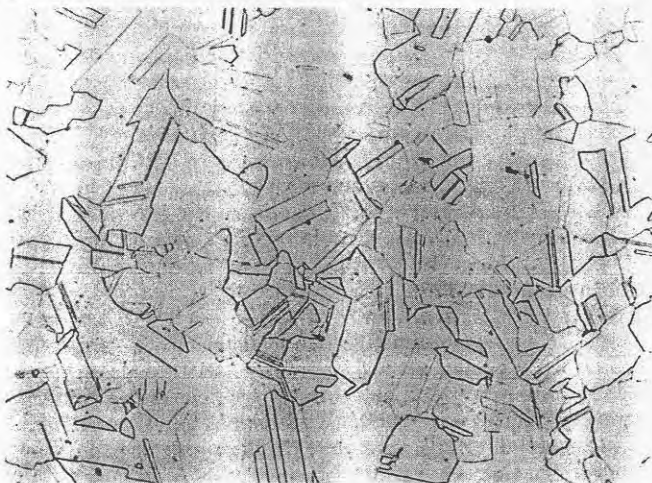


Fig. 1 Mill annealed RA-330 with resultant grain size of about ASTM 5. Etchant: Mixed acids — 25 parts HCl, 19 parts alcohol and 7 parts HNO₃. Magnification 100X (enlarged 20%).

It is rather well recognized that coarse grain size improves rupture and creep strength at elevated temperatures⁴. Alloys intended for elevated temperature structural service, where creep or rupture are the limiting factors, are often annealed at high temperature both to dissolve the carbides and to increase grain size. ASTM 5 or coarser is often specified for construction requiring the highest allowable design stresses. It is possible that some

of the strength increase attributed to grain size, achieved by a high temperature anneal, comes from the effect of that anneal on the nature of the grain boundary itself (misorientation angle).

If creep or rupture were the only mechanical properties of interest, all heat resistant alloys would be supplied in the solution annealed condition. However, as mentioned, thermal fatigue is one of the most common failure modes of industrial heating equipment. Thermal fatigue resistance is also influenced strongly by grain size, but, in contrast to rupture strength, it is the finer grain material which is superior. The influence of grain size on thermal fatigue has been investigated by others⁵. At Rolled Alloys the importance of grain size became known through numerous laboratory investigations of field failures during the 1950's. Grain size has been found to influence not only thermal fatigue but also the combined effects of thermal cycling and carburization.

As fabrications of RA-330 and RA-333 are often intended for thermal cycling applications, Rolled Alloys supplies most product forms of these alloys in the mill annealed condition. Experience of this company has been that, by aiming at a medium-fine grain size, an optimum combination of strength and thermal fatigue resistance is achieved.

Nature of Thermal Fatigue

Two inherent physical properties of austenitic heat resistant alloys contribute to thermal fatigue failure.

The first is thermal expansion. Expansion coefficients vary with alloy composition, but any of these alloys will expand from $\frac{3}{16}$ " to $\frac{1}{4}$ " per ft when heated from room temperature to 1800°F. Over the length of a radiant tube or muffle that can be a lot of expansion, and subsequent contraction, to be accommodated by careful design and installation.

The second characteristic is poor thermal conductivity. A good average value for conductivity of an austenitic heat resistant alloy is about $\frac{1}{4}$ that of carbon steel and $\frac{1}{50}$ that of copper. Such low thermal conductivity means that truly uniform heating and cooling of any piece of heat resistant alloy equipment is unlikely in normal service.

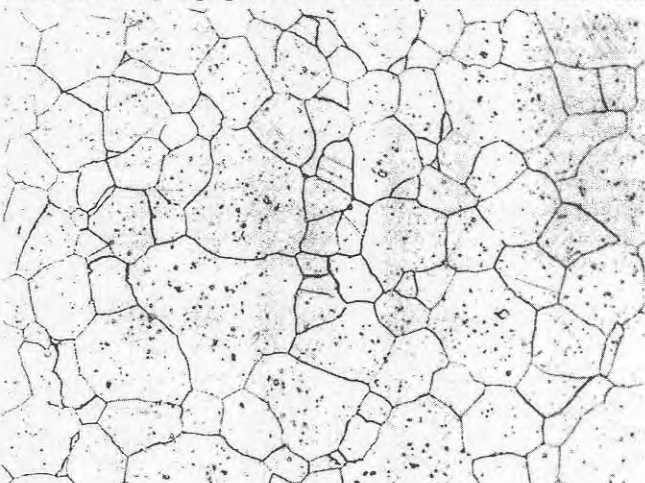


Fig. 2 Mill annealed RA-333 with resultant grain size of about ASTM 5 exhibits higher volume of carbides than RA-330 because of higher degree of alloying elements. Etchant: Mixed acids. Magnification 100X (enlarged 20%).

Failure to recognize this fact in the design and installation of such equipment costs dearly. Thermal gradients are the rule in any equipment involved in thermal cycling and even in many furnace components which operate at more or less constant temperature.

A combination of thermal gradients with high expansion coefficient can result in thermal strains of tremendous magnitude — far greater than the strains from

mechanical loading.

While mechanical stresses can be calculated and allowable loads determined with some assurance from published creep-rupture data, information on thermal gradients is less easily obtained. Indeed, the existence of large thermal stresses may not even be suspected until the alloy equipment warps.

Thermal fatigue failures are more likely in those fixtures or bar frame baskets which are subject to liquid quenching. Clean hardening equipment, because of the number of heat/quench cycles possible per day, almost invariably ends its useful life by thermal fatigue cracking.

In heat resistant alloy bars, thermal fatigue failures may begin internally, giving no notice of metal deterioration until the basket or fixture suddenly breaks in service or when straightening is attempted.

Figs. 3-6 illustrate the combined effects of bar diameter and grain size upon thermal fatigue and carburization. The samples are from a $\frac{3}{8}$ " diameter bar frame basket, lined with wire mesh and having $\frac{1}{2}$ " diameter bars mounted horizontally above the frame work for handling. Material was a 35Ni-18Cr-1.5Si alloy similar to RA330, but not supplied by Rolled Alloys.

This basket was used in a heat treating cycle which consisted of neutral hardening from 1550°F, oil quench, wash, and temper 980-1150°F followed by a soluble oil quench. After the baskets had warped beyond use they were given to an alloy fabricator for straightening. The $\frac{3}{8}$ " diameter bar frame was easily straightened, while the $\frac{1}{2}$ " diameter bars broke readily in a brittle manner. These $\frac{1}{2}$ " bars were found to be magnetic, a condition which usually indicates carburization or severe oxidation.

Metallography revealed that the $\frac{1}{2}$ " diameter bar was a maze of internal intergranular thermal fatigue cracks (Fig. 3) and, in addition, was rather carburized (Fig. 4). The chromium carbides form a semi-continuous network on grain and twin boundaries as well as being distributed throughout the matrix. Thermal fatigue cracks follow the grain and carbide-matrix boundaries. These crack surfaces and, to some extent, the carbides subsequently oxidized. Grain size of this $\frac{1}{2}$ " diameter bar is about ASTM 2-4, somewhat coarser than optimum for bar frame baskets.

The $\frac{3}{8}$ " diameter bar, having some 44% less cross-sectional area than the $\frac{1}{2}$ " bar, was able to heat and cool more uniformly throughout its section, hence suffered less thermal strain during each heat treat cycle. As a result, these smaller bars showed little internal damage or internal carburization (Figs. 5 and 6). This is a striking illustration of the relationship between section thickness and service life in liquid quenching applications.

The ASTM 5 or finer grain size of the $\frac{3}{8}$ " bar, which must have had a positive influence, would be considered quite acceptable for heat treating service.

Internal thermal fatigue is the normal (but not well recognized) failure mode for those bar baskets or fixtures used primarily for through hardening of carbon or alloy steels. Failure manifests itself by sudden breakage in service or during straightening with no evidence of ductility. The cracks grow both longitudinally and transversely. A branched longitudinal crack may run down the center of the bar, much like an internal forging burst. It would seem that this crack should grow and split the entire bar lengthwise, but before it does so a series of evenly spaced transverse cracks usually grow to fracture. These internal thermal fatigue cracks, shown as a maze of intergranular cracks in Fig. 3, appear to begin near the center of the bar and grow outward until only a thin rim of sound metal remains. A room temperature transverse fracture of such a bar reveals a rough, blackened area in the center surrounded by a rim of bright metal (Fig. 7) representing the sound portion of the metal.



Fig. 3 Internal thermal fatigue cracks in cross section of $\frac{1}{2}$ " diameter RA-330 bar frame basket.



Fig. 4 Microstructure of sample shown in Fig. 3 evidences semi-continuous network of chromium carbides on grain and twin boundaries as well as being distributed in the matrix. Etchant: Mixed acids. Magnification 500X (reduced 5%).

Fig. 5 Little internal damage is evident in cross section of $\frac{3}{8}$ " diameter RA-330 bar frame basket.



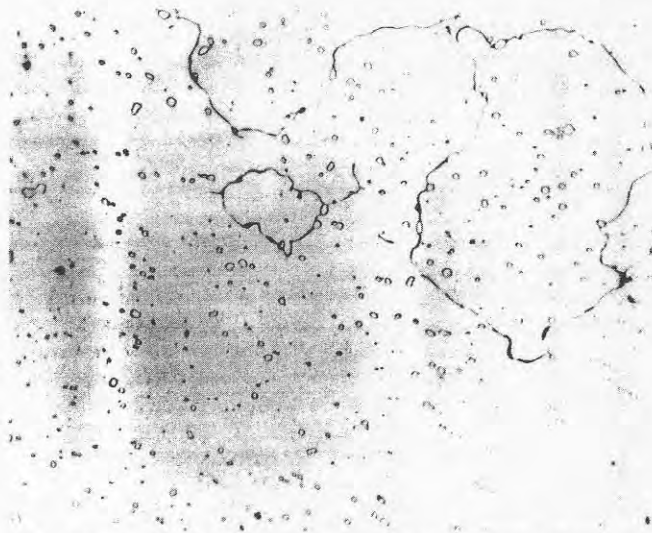


Fig. 6 Microstructure of sample shown in Fig. 5 shows little internal carburization. Etchant: Mixed acids. Magnification 500X (reduced 5%).

The only outward sign that such failure is about to occur is a series of circumferential contractions or "rings" spaced periodically along the bar. Each such contraction represents a plane where internal fatigue cracks have nearly reached the surface. Sighting along the bar at a light source is the easiest way to see these rings. The bar may be readily broken at each such ring and will reveal a fracture surface similar to that shown in Fig. 7.

These failures have been observed in bars ranging from ½" diameter upwards. Also, the longer the bar, the quicker the failure. The failures are a result of the time lag required for the interior of the bar to reach the same temperature as the surface during both the heating and the quench cycles. When the cold bar is placed in the furnace the outside surface reaches temperature first and expands both lengthwise and in diameter, thus placing the interior in a state of approximately triaxial tension. The reverse occurs during the quench. Obviously, the larger the bar, the greater the temperature difference and the higher the stress caused by differential thermal expansion.

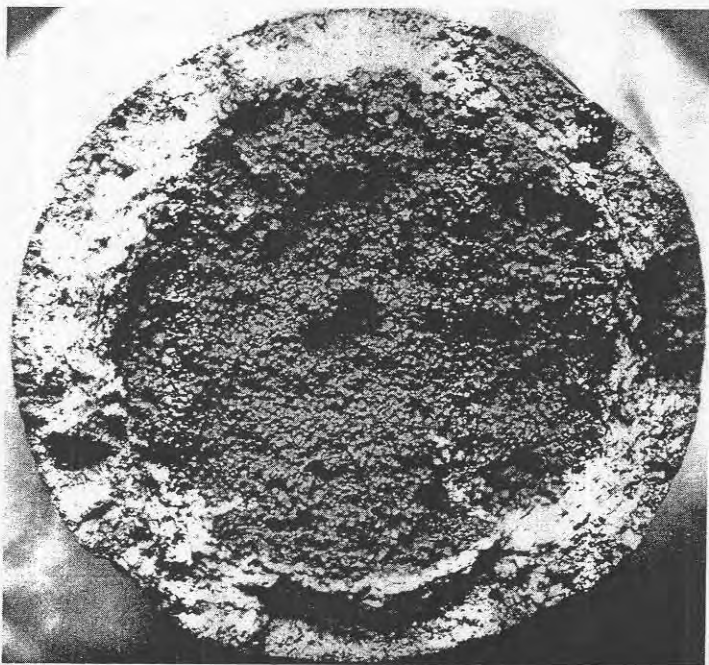


Fig. 7 Fracture surface of ½" diameter RA-330 bar frame basket.

Although the Investigation File at Rolled Alloys contains laboratory analyses of such failures dating back to the mid-1950's, only recently have we noted a formal discussion of this internal failure mechanism in a book edited by C.S. Smith⁶. Apparently similar internal fractures used to occur in steel bars and were of economic consequence quite some year ago. An intelligent explanation, almost entirely applicable to present failures, of this problem was given by Jean Jacques Perret in his *L'Art du coutelier* — published in 1771.

How to reduce thermal fatigue failure? Where mechanically practical, use smaller bar diameters or flat sections rather than large diameter rounds. Stronger alloys, provided that their strength is not achieved by grain coarsening, also help. The substitution of an alloy such as RA-333 may permit using thinner cross-sections, thus reducing thermal strain while maintaining comparable mechanical load bearing ability.

Corrosive Media

Effects of Carbon

Occasionally some confusion exists when alloy equipment used in "neutral" atmosphere is found to be carburized. When this neutral atmosphere is generated from natural gas, and is intended to be in equilibrium with steel of 0.3-0.5% carbon, it will be carburizing with respect to such low carbon steel as AISI 1008. It may also carburize heat resisting alloy to some degree.

Carburization of high temperature alloy components in heat treating service can reduce room temperature ductility to zero. This, naturally, leads to brittle failure as the equipment is subject to normal handling and abuse at ambient temperatures, or when straightening is attempted. However, carburization does not seriously reduce the material's resistance to thermal fatigue. This is probably because ductility at elevated temperature, where thermal fatigue damage occurs, remains quite good, even in heavily carburized alloy. Data have been published showing that at 1600 and 1800°F, highly carburized heat resistant alloys have hot ductility comparable to the room temperature ductility of uncarburized material⁷.

Increasing carbon content also lowers the melting point of an alloy. A combination of high local temperatures and high carbon occasionally results in some component melting. Radiant tubes are most prone to melting during carbon burn-out. The furnace thermocouple may read only 1700°F or so but burning soot deposits can raise the temperature in some areas of a radiant tube to the point that it carburizes severely and begins to melt. Once melting begins, carburization is more rapid and a whole section of the tube may melt catastrophically. Fig. 8 illustrates a vertical alloy radiant tube which excessively vigorous soot burn-out has destroyed.

The rate at which a heat resistant alloy carburizes depends upon the degree of protection provided by the oxide scale formed in service, upon the diffusion rate of carbon in the alloy and upon the solubility of carbon in that alloy.

Numerous studies since the 1940's have explored the relationships between carburization resistance and nickel, chromium and silicon levels. The current state of the art has been well summarized by both D.B. Roach¹⁰, and by J. Blackburn¹². In general, chromium retards carbon diffusion rate but increases maximum carbon content near the surface; nickel lowers the carbon gradient and reduces maximum carbon levels; and silicon is the one element which most effectively controls carburization in high temperature alloys. Sufficiently high silicon levels can almost

eliminate carburization in laboratory tests of samples under atmospheres similar to those used in industrial carburizing. However, should the carburizing gas contain no partial pressure of oxygen to form a protective oxide scale, which is sometimes the case in laboratory tests using methane-hydrogen or methane-argon atmospheres, the silicon cannot perform its function in the scale and will therefore have far less influence on carburization behavior.

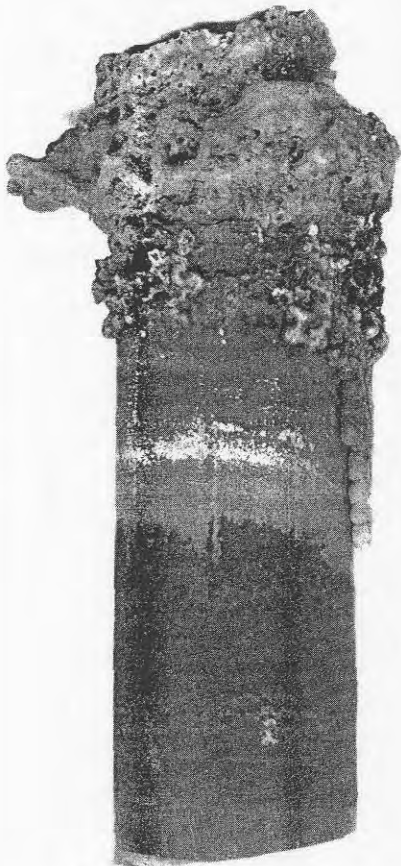


Fig. 8 Destruction of vertical alloy radiant tube due to sooting and melting upon carbon burn-out.

In practice, alloys such as RA-330 and RA-333 find extensive application in carburizing environments whereas lower alloys, such as 310 or the common stainless grades, do not possess useful resistance to carburization. The relative behavior of these three alloys is illustrated in Table II by some unpublished work performed by Surface

Table II Carbon Analyzed in 0.02" Surface Cut from Plate Samples Gas Carburized at 1750°F

Alloy	Weight % Carbon
RA 333	0.344
RA 330	0.443
310	3.92

Combustion Div., Midland-Ross Corp. Plate samples were exposed at 1750°F for a total of 4300 hours to three different atmospheric conditions as follows: approximately 860 hours in endothermic plus natural gas at 1.0-1.2% carbon potential relative to iron, 3010 hours in nitrogen and 430 hours air burnout at 100°F reduced temperature.

One of the inadequacies of even the best laboratory carburization tests is that they do not take into account the influence of thermal cycling or mechanical stress upon carburization rate. Both rapid temperature changes and high temperature creep of alloy components tend to disrupt or spall the oxide scale, reducing its ability to protect the underlying metal from carburization. Careful analysis of alloy fabrications which have been used in actual, well defined service is a necessary adjunct to laboratory tests.

Effects of Salts

Neutral heat treating salts can pose one of the more interesting hot corrosion problems. The molten salts themselves, mixtures of alkali and alkaline earth chlorides, carbonates or nitrates, are usually not particularly corrosive to wrought alloys. Hot vapors of these salts, on the other hand, are extremely aggressive and will chew away any heat resisting alloy at the salt-air interface and for several inches above the salt bath level. Of course, this attack on fixtures, over-the-top heating electrodes or on alloy pots themselves is visible and the operator may readily judge when these items need replacement.

The less obvious problem is that surprisingly rapid failure may occur in the alloy salt pot itself if any salt should be present on the outside surface near the heating elements or burners. The combination of high temperature and salt vapors causes rapid, voluminous scaling with failure in a very few weeks or months. In more than one case failure to remove old neutral salts from the refractory surrounding externally heated alloy pots has caused a newly installed salt pot to fail within three days.

The corrosive effects of salt fumes have been described in metallurgical literature for decades,^{8,9} but the task of disseminating this information to those involved in salt pot operation or maintenance is far from complete.

Effects of Low Melting Point Metals

Low melting temperature metals can also be a source of mysterious failures. Molten copper and silver brazing alloys, even in small amounts, have destroyed many expensive alloy muffles or retorts. On clean, hot austenitic materials, molten copper, in particular, will quickly penetrate the grain boundaries and has been known to pass right through the alloy without leaving a visible hole. Metal under thermal or mechanical stress can develop a small crack through which the (usually flammable) protective atmosphere escapes and burns like a torch. The resultant local over-temperature may severely oxidize or melt the surrounding area, making subsequent failure analysis an interesting procedure.

Generally, ferritic alloys are much more resistant than austenitic alloys to attack by brazing alloys. Within the austenitic family the rate of attack tends to be somewhat more severe with the higher nickel alloys.

When brazing is performed under some atmosphere generated from natural gas there is usually enough CO, CO₂, or H₂O present to develop a protective oxide scale on the heat resisting alloy muffle, wire mesh belt or other fixture. This scale prevents, to some degree, wetting by minor spillage of brazing alloy from the workpieces. Unless rather large amounts of brazing alloy are spilled, the heat resistant alloy components will generally give normal service life before eventual failure from creep distortion or cracking from thermal cycling.

Problems may occur when brazing in dry hydrogen or cracked ammonia. With sufficiently low dew point such

atmospheres are reducing to chromium, and the heat resistant alloy muffle will remain bright and clean inside. Under these conditions it takes little copper or silver braze to wet and penetrate or crack the austenitic alloy. For example, an RA-330 muffle was used for silver brazing at 1600°F under hydrogen atmosphere. The muffle interior was visibly bright and clean with a large amount of silver braze spilled over the bottom. Reaction of this braze alloy with the muffle formed the detrimental compounds shown in the photomicrograph, Fig. 9. The reaction proceeded from the inner surface through about two-thirds of the wall thickness.

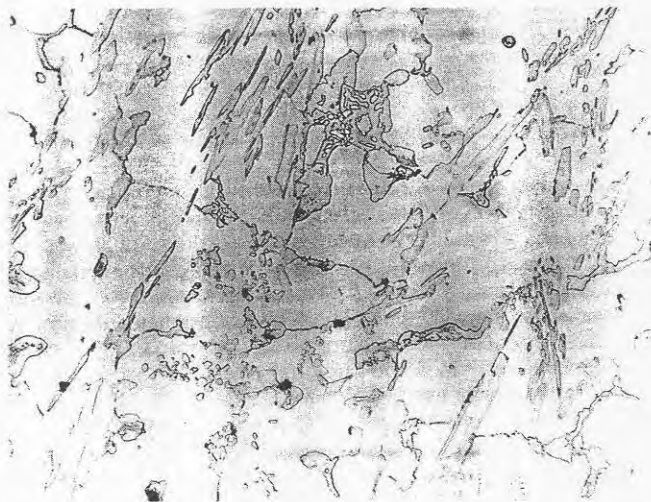


Fig. 9 Silver brazing alloy reaction with furnace muffle made of RA 330 (35% Ni, 19% Cr, 1.25% Si) formed low melting-point compounds through two-thirds of the muffle wall thickness. Etchant: mixed acids. Magnification 100x (reduced 25%).

One way to prevent such damage to muffles or retorts is to use a tray or waster sheet in the bottom to collect the braze spillage and protect the expensive alloy muffle. A 26% Cr ferritic alloy RA-26-1 is usually suggested, for this purpose, the basic criterion being that the alloy remain ferritic at operating temperature. Even mild steel can be penetrated intergranularly by molten copper, since it is fully austenitic at or above copper's melting point.

Attack by copper base alloys is not limited to brazing operations. Copper and bronze powders are often used to infiltrate powdered iron parts. During the sintering process a certain amount of copper eventually sifts down to the bottom of the muffle and, particularly under hydrogen atmospheres, may reduce service life of the muffle.

Some other low melting temperature metals which may come in contact with heat resistant alloys are aluminum, the zinc die casting alloys and lead. Molten aluminum will dissolve any commercial nickel or iron base alloy. Metals used in contact with molten aluminum must be protected by some type of applied oxide coating. The life of such equipment will be governed by coating integrity. Zinc or zinc die casting alloys will also dissolve or embrittle most available alloys. Commercially pure iron, type 316 stainless steel and Hastelloy C-276 are used with reasonable success in steel mill galvanizing equipment submerged in molten zinc at just above its melting point. Immersion heating tubes for zinc die casting pots are often fabricated of type 309 stainless steel, but these require plasma sprayed oxide coatings to protect against dissolution or cracking from zinc.

Molten lead, by contrast, may be contained nicely by fabricated pots of an alloy such as RA-330 for heat treating service. Eventual failure may occur by attack from lead oxide at the lead-air line. Occasionally this attack is aggravated by mild carburization or sulfidation from the carbonaceous cover used to prevent oxidation of the lead. Service life may be extended by making the pot double thickness at this lead-air line, as well as by use of virgin lead and good maintenance procedures.

It is important that fabricated lead pots be joined with a weld filler similar in composition to the base metal. If dissimilar alloys are in contact with the same molten metal, it is possible for one of the alloys to be preferentially attacked by the molten metal¹¹. One such failure involved a large RA-330 lead pot which was fabricated by using a high nickel welding rod containing approximately 2% columbium. After some period of service the pot failed adjacent to the welds, and the weld beads, strangely enough, could be picked out with a knife blade. Upon chemical analysis, this former nickel-chromium-columbium weld bead was found to have transformed during service into a lead-5% columbium bead of very low chromium and nickel contents. Where the nickel went was not known, but it was indeed dissolved and then replaced by lead. No such failures have been reported when the matching filler metal, RA-330-04, has been used to fabricate RA-330 lead pots.

References

1. H. Klouman, "Heat Treating Equipment", *The Book of Stainless Steels*, ed. Ernest E. Thum, 2nd ed. (Cleveland: ASM, 1935) p 644
2. H.S. Avery, "Cast Heat-Resistant Alloys for High-Temperature Weldments", *WRC Bulletin 143* (New York, Aug. 1969) pp 55-59
3. *Ibid* pp 55-56
4. F. Garofalo, *Fundamentals of Creep and Creep-Rupture in Metals* (New York, 1965) pp 27-31, 128-129
5. Franklin, Heslop and Smith, *Journal of the Institute of Metals*, Vol. 92 1963-64 pp 313-322
6. *Sources for the History of Steel 1532-1786*, ed. Cyril Stanley Smith (Boston: M.I.T. 1968) pp 71-72
7. D.E. Wenschhof and J.A. Harris, "The Influence of Carburization on the Mechanical Properties of Wrought Nickel Alloys", *Corrosion* 77 Paper No. 9
8. H. Klouman, *op. cit.* pp 638-640
9. J.H. Jackson, "Cast Alloys for Salt-Bath Heat Treating", *Alloy Casting Bulletin* Number 16, Nov. 1952
10. D.B. Roach, "Carburization of Cast Heat-Resisting Alloys", *Corrosion* 76 Paper No. 7
11. "Corrosion Resistance of the Austenitic Chromium-Nickel Stainless Steels in High Temperature Environments", *The International Nickel Co., Inc. (New York: 1963) Bulletin A-320* p. 10
12. J. Blackburn, *Current Status of Carburization Testing and Assessment*, *Materials Performance*, December 1977 pp 24-29