Oxidation Rates of Some Heat Resistant Alloys

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Abstract

Cyclic oxidation testing of several heat resistant alloys was carried out at 1093 and 1149°C for times up to 3,000 hours. The quantitative results, coupled with extensive service history for the established alloys, provide a useful guide to anticipated performance of newly developed grades. Maximum practical use temperature is to some extent a function of section size, thin sheet being more quickly depleted of elements used to form the protective scale. Metallurgical factors influencing oxidation rate include grain size as well as the alloying elements silicon, manganese, molybdenum and columbium. Some comparisons are made between laboratory results and service performance.

Introduction

Laboratory oxidation testing is performed as one phase of the evaluation of newly developed heat resistant alloys. The results are used to compare the newer grades with existing materials for which both laboratory results and service experience exist. For the laboratory work to have engineering utility the testing should to some degree, approximate anticipated service conditions for the class of alloy involved. The alloys studied here are intended for purposes as heat treating furnace internals, coal nozzles for utility boilers, kilns, fluidized bed combustors and other thermal processing equipment. Appropriate test conditions include cyclic rather than isothermal oxidation, specimen thickness in the range commonly used in service, 3 to 13mm (1/8 to 1/2 inch) and a test duration of at least 1,000 hours. The effect of grain size as an important variable is shown through examination of metal returned from actual service.

Procedure

The current program was carried out using flat specimens in the range 4 - 7mm thick, prepared by wet sanding on 400 grit paper, and placed in porcelain crucibles. Six crucibles at a time were held in a tray fabricated of 3.2mm sheet, either RA333® (N06333) or Haynes® 214 alloy. The tray was placed in a Lucifer electric box furnace, 230 X 230 X 460mm (9 X 9 X 18 in) held at temperature, and removed weekly. In order to compensate for temperature gradients within the furnace the tray was reversed end for end each cycle. Immediately upon removal from the furnace the crucibles were covered in order to retain all spalled oxide. After air cooling to room temperature, each crucible together with its contents was weighed to within 0.1mg. The original specimen area was used for calculation of weight gain in mg/cm^2.

1093 and 1149°C

Weight gain data for eight different alloys are shown in Figs 1 and 2. At 1093°C the 25% chromium grade HR-120 was one of the three best studied. A 56°C increase in test temperature resulted in accelerated oxidation of this grade considerably, probably due to the detrimental effect of 0.6Cb on oxidation resistance. Three high silicon alloys, N06333, S35315 and N08330 showed much less effect of temperature on oxidation

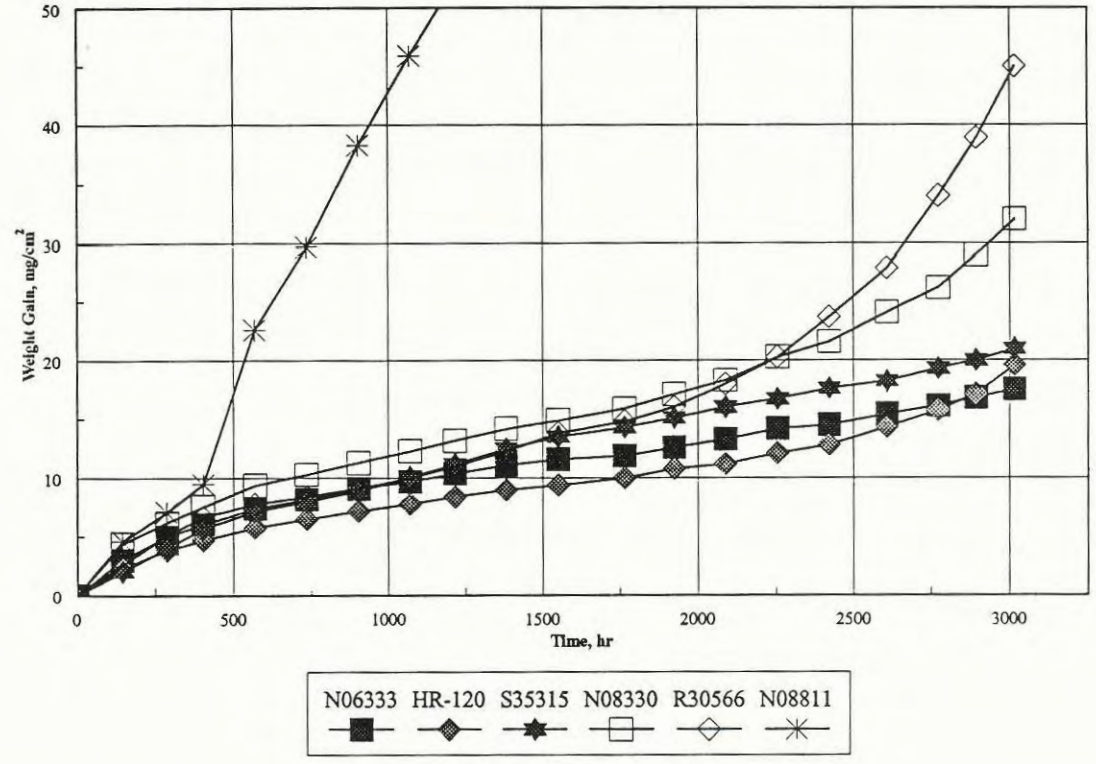

Fig. 1 Cyclic Oxidation, 1093°C (2000°F)

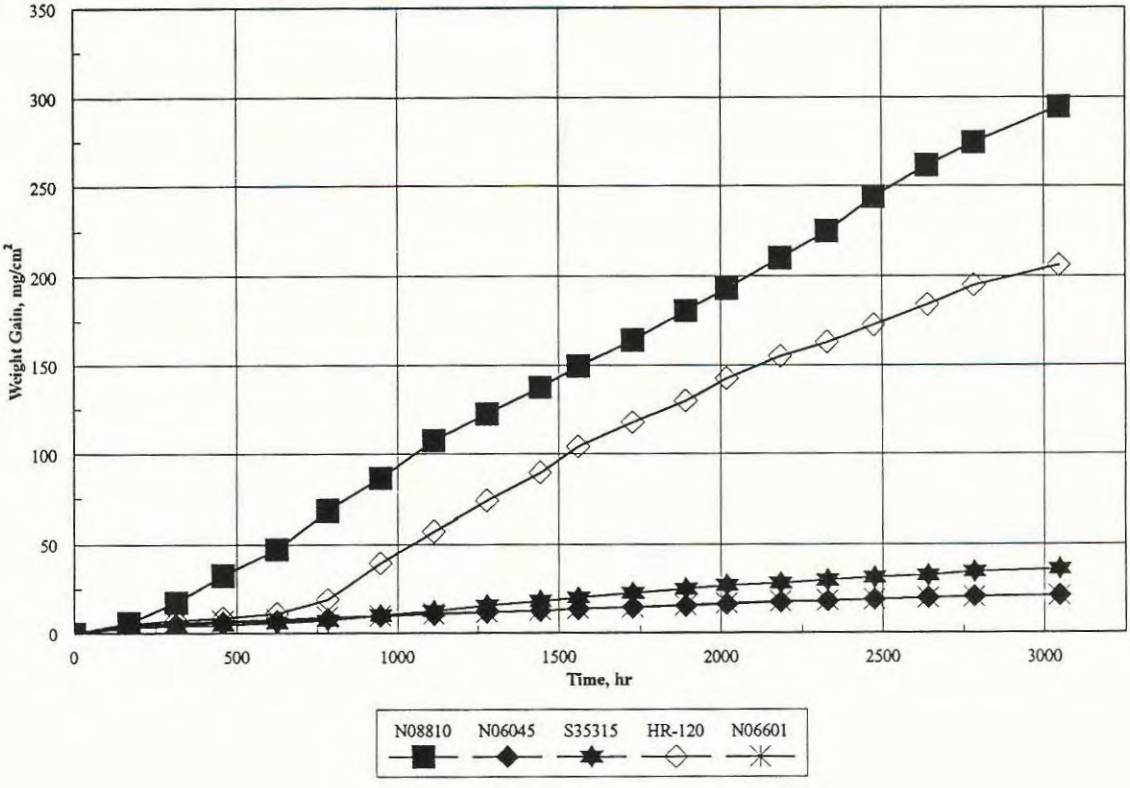

Fig. 2 Cyclic Oxidation, 1149°C (2100°F)

rate, Fig. 3. All three also developed relatively thick scales with internal oxide penetration. The low Si, 20Cr materials N08810/N08811 scaled heavily at both test temperatures.

To put this data in perspective, consider two grades, N08330 and N06333 commonly used for industrial heating equipment. Figure 4 shows an electrically heated retort of N08330 after some 2100 hours at process temperatures from 700 to 1150°C, primarily 1120°C. As temperatures measured are process temperatures, the retort wall itself would have been somewhat hotter. The 4.76mm (3/16 in) wall is rather pitted from one-sided oxidation, nevertheless it was primarily excessive creep deformation that ended the useful service life of this equipment.

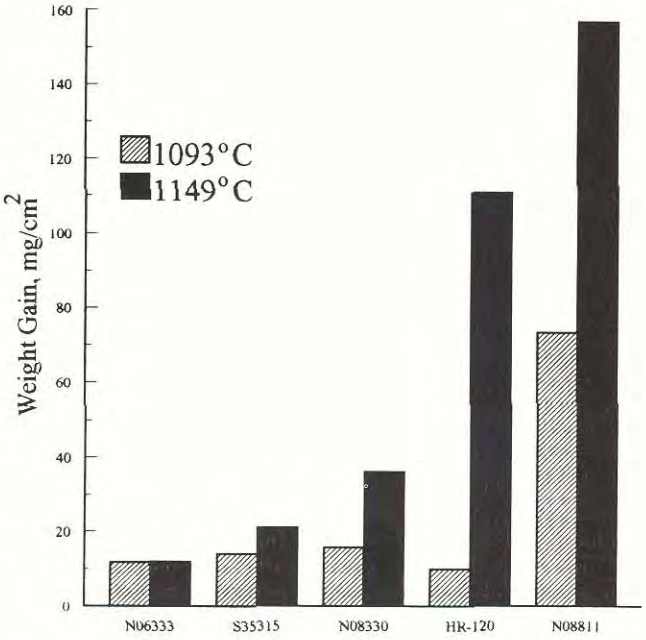

Fig. 3

Effect of Temperature on weight gain, at 1640 hrs.

Table I

Composition of Test Materials, wt %

Alloy	Cr	Ni	Si	Mn	Mo	Co	W	C	Fe	Other
N06333	25.17	44.79	.99	1.59	3.08	2.76	3.24	.04	18	--
N06045	27.0	46.25	2.76	.29	--	--	--	.086	23.3	--
S35315	25.1	35.0	1.39	1.3	--	--	--	.043	37	.155N .05Co
HR-120	25.08	37.44	.57	.66	.59	.76	.38	.05	33	.62Cb .25N
N08330	19.14	35.28	1.31	1.54	.15	--	--	.05	42	--
N08334	19	35	.9	5.2	--	--	--	.22	39	--
N08810	20.3	30.5	.11	.81	.29	--	--	.08	46	.13Ti .44Al
N08811	19.81	30.81	.50	1.23	.23	--	--	.07	46	.53Ti .50Al
R30556	22.05	20.79	.48	.96	2.98	18.51	2.56	.11	30	.7Ta .007La
N06601	22.9	60.5	.17	.22	--	--	--	.05	14.1	1.33Al .44Ti
N06082	19	72	.2	3	--	--	--	.02	2.5	2.7Cb .5Ti
N08367	20.5	24	.4	.3	6.2	--	--	.02	48	.2N
N06625	22	61	.4	.2	8.5	--	--	.04	4	3.5Cb

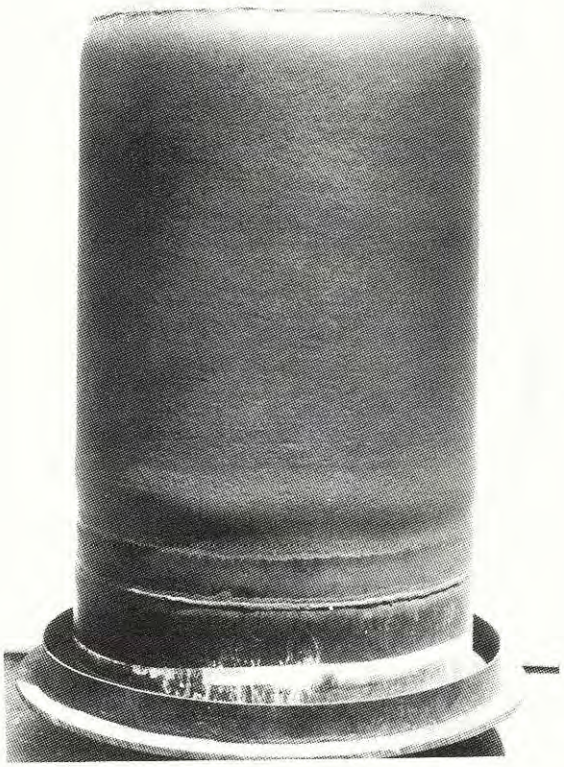

Fig. 4

N08330 retort [1] 660mm dia 1220mm high, 4.76mm plate after 2100 hr operation 700-1150°C, primarily 1120°C.

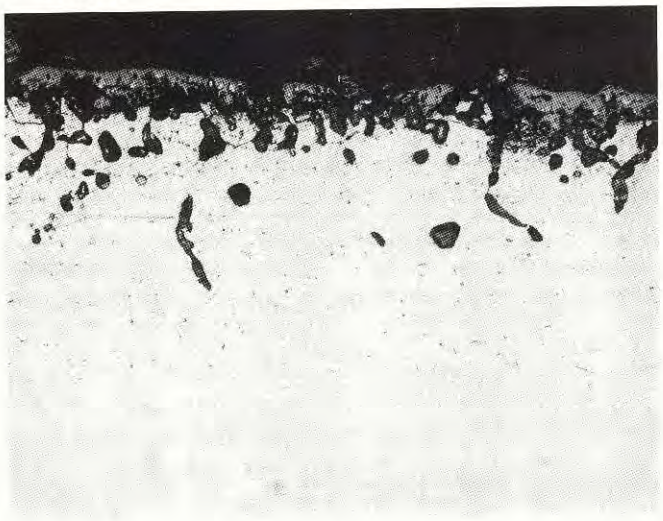

Fig. 5 Unetched 200X

Internal oxidation, N06333 after 3012 hr 1093°C.

Fig 5 shows internal oxidation of the N06333 sample after test at 1093°C, and Fig. 6 the surface condition of 3mm (11ga) N06333 from a copper brazing muffle. Natural gas fired outside with an H_2 - N_2 atmosphere inside, this muffle served 8 months (5800 hr) at a process temperature 1120°C. High production levels required higher muffle wall temperatures. Based on voids at grain boundary triple points causing through-wall porosity, and the glazed appearance of the scale, estimated temperature would have exceeded 1260°C (2300°F) for some period of time.

Fig. 6 Unetched 100X

N06333 muffle.

Test Duration

The oxidation behavior of commercial heat resistant alloys is a sufficiently complex process that anticipating long term behavior on the basis of short term data is an uncertain matter. This can be illustrated by Figure 7, the results of cyclic oxidation carried out for more than 10 months. [2] The relative performance of alloys RA333 (N06333) and 601 (N06601) is entirely different after 6200 hours than it was at 600 hours.

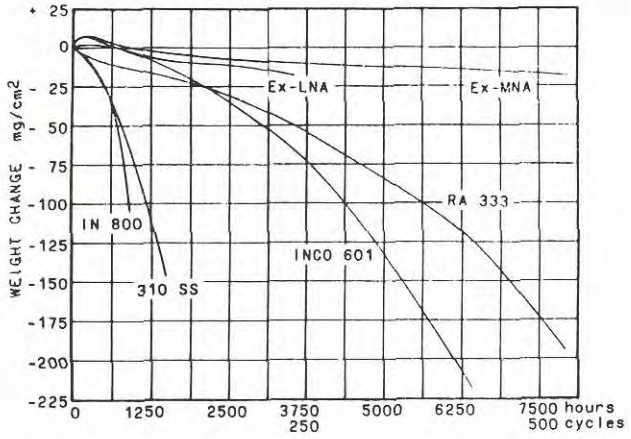

Fig. 7

Still-air cyclic oxidation resistance of high temperature alloys at 1038°C (1900°F).

These results, and the authors' various observations of rapid increase in oxidation rate at times ranging from 500 to 2600 hr, both at 1093°C (2000°F) and 1149°C (2100°F), support an inclination to carry out oxidation test series for at least 1000 hr, and preferably 3000 hr.

Section Thickness

Thickness of the material being tested matters because it relates to the total amount of scale of the material being tested forming elements (Cr, Si, Al) available to form a protective scale, and to reform that scale as portions of it are lost by spalling. In the case of FeCrAl-based oxide dispersion strengthened alloys the time to breakaway oxidation (caused by Al depletion) can be calculated as a function of wall thickness. [3]

For the chromia forming NiCrFe alloys considered here much the same phenomenon occurs, although perhaps not so amenable to calculation. In practice, a retort fabricated of RA330® (UNS N08330) plate may function for years at 1149°C (2100°F) without enough thickness loss from oxidation to impair function. However 0.13mm (0.005 in) foil of N08330 may be entirely consumed after a week at that same temperature.

Figure 8 shows weight gain for six N08330 specimens ranging from 0.13 to 9.5mm. (0.005 to 0.375 in) after one 97 hr cycle at 1149°C. In another cycle the foil sample was oxidized through. By 1730 hr of weekly cycling the remaining five samples formed three groups by weight gain, Table 2.

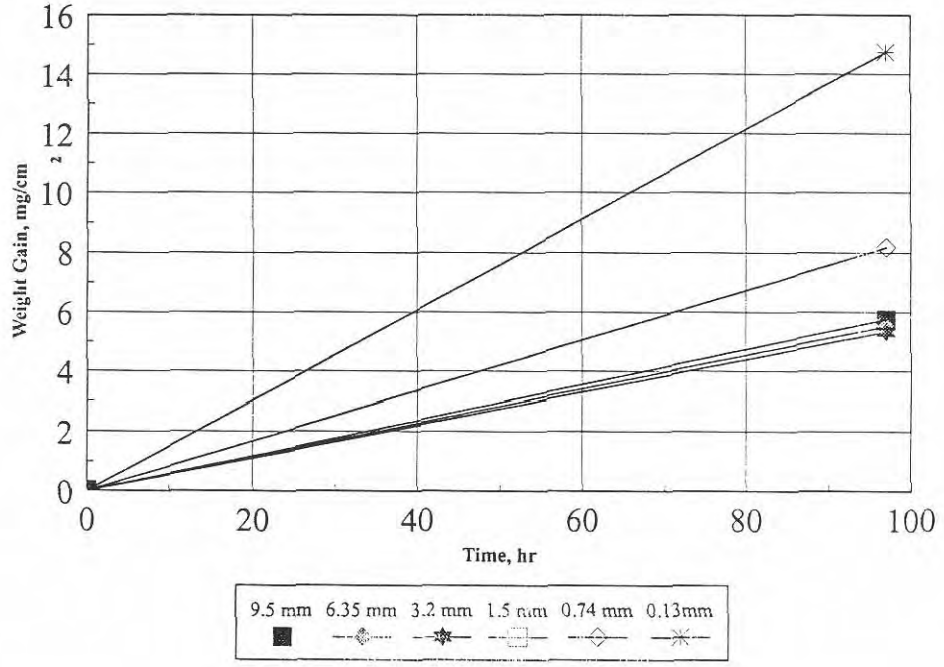

Fig. 8 1149°C (2100°F) isothermal oxidation versus thickness, N08330

Table 2 Oxidation vs Thickness

specimen thickness, mm	weight gain mg/cm^2
9.5	33.0
3.2 - 6.3	40.9 - 39.2
0.7 - 1.6	44.0 - 43.7

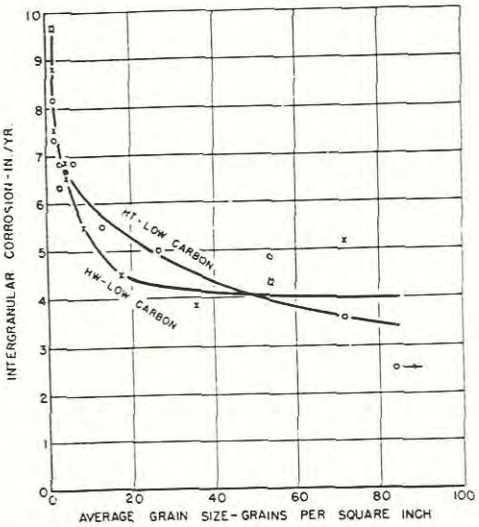

Fig. 9

The effect of grain size on the depth of intergranular corrosion attack of low carbon cast Ni-Cr-Fe alloys.

Grain Size

It has long been recognized that a fine grained heat resistant alloy generally outperforms the same alloy chemistry in a grain coarsened condition, with respect to environmental attack. The enhanced short-circuit diffusion of chromium with increased grain boundary area [4] improves the ability of the scale to form and to re-heal damage. As a result, the oxidation resistance of both chromia and alumina [5] forming alloys is a strong function of grain size.

One example is the Alloy Casting Institute study of the grain size effect on intergranular corrosion rates of low carbon cast Ni-Cr-Fe alloys in molten chloride salts [6]. Samples were exposed 50 hr at 871°C (1600°F) 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 in Figure 9.

The effect of grain size on long time oxidation of S30400 stainless is similar. Figure 10 shows part of a type 304 stainless steel "belly band", 11.5 X 38mm in cross section, used to reinforce corrugated S30908 inner covers for batch annealing carbon steel coils.

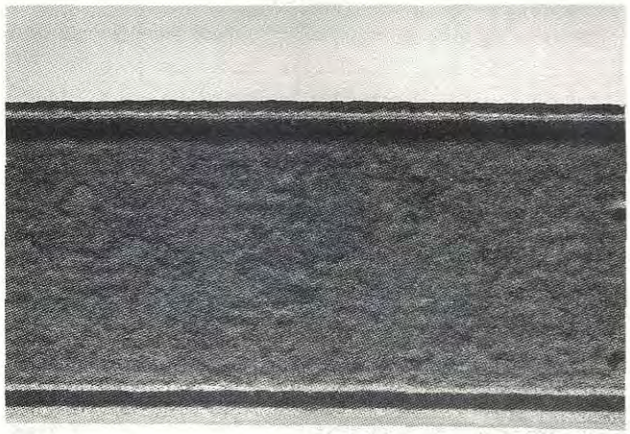

Fig. 10 Oxide grooves in S30400 reinforcing band 0.85X

Service conditions were products of combustion of natural gas with excess air, at 870°C (1600°F) for perhaps five years. The flat bar for this band was produced by shearing strips from 12.7mm (1/2 in) plate, the edges being heavily cold worked by the shearing operation. Metal loss due to oxidation would be 0.6mm per side over most of the band, with a narrow zone of deep attack parallel to, and 2.5-3mm from, the sheared edge, Figure 11.

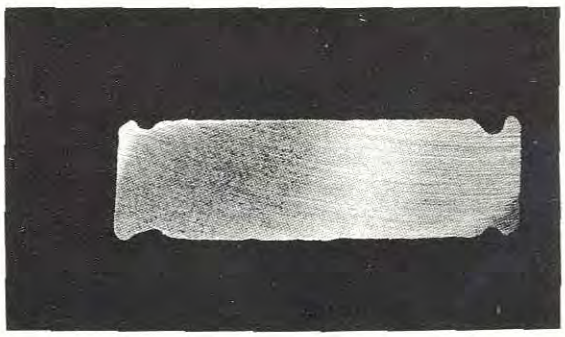

Fig. 11 Reinforcing band cross section 1.4 X

Grain size of the bulk metal measured ASTM 7. Due to recrystallization in service metal near the sheared edges had grains as fine as ASTM 8. A short distance

back from the edge, coincident with the heavily attacked zone, cold work (from the shear) in the critical range caused recrystallization to grain size as coarse as ASTM 4. The relation between metal wastage and grain size is shown in Figure 12.

Metal loss at the corners was greater than might be expected, and it may be attributed to the effect of geometry. Scale adhesion, hence oxidation resistance, is poorer in areas of sharp curvature than on flat surfaces [7].

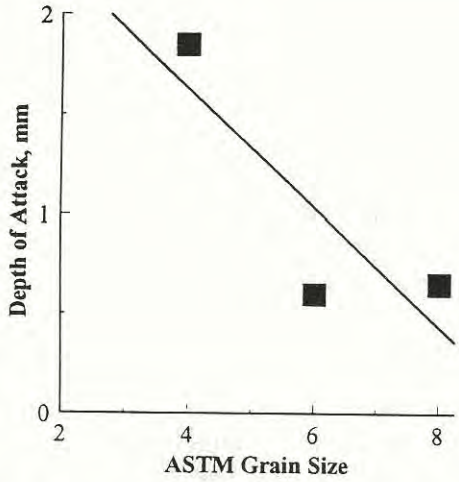

Fig. 12 Oxidation vs grain size, S30400.

Effect of Mn, Cb and Mo on Surface Stability

Cb and Mo are well known [8, 9] to impair high temperature surface stability, and manganese may be restricted for that same reason. [10] In welding nickel alloys, the need to avoid hot cracking has often meant the development of weld fillers which compromise some oxidation resistance for improved weldability. N06082 uses 3%Mn and 2.7%Cb for this purpose, and N08334 5.2%Mn. Oxidation resistance of these grades at 1093°C (2000°F) compared with the base metal N08330, is shown in Fig. 13.

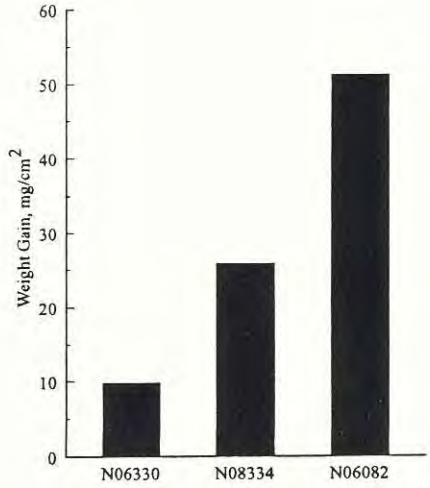

Fig. 13 1093°C, 500 hr, 20 hr cycles

The result of welding N06600 with N06082 for extreme temperature service is shown in Fig. 14, the longitudinal weld in a 9.5mm (3/8 in) wall, 203mm (8 in) dia rotary retort operated above 1200°C. While the base metal is pitted from oxidation, the weld bead has completely oxidized in the hottest zone. Poor temperature control is an issue here. However autogenously welded N06600 has performed satisfactorily, as has S35315 welded with a new matching filler containing no Cb or Mo, and fairly low Mn.

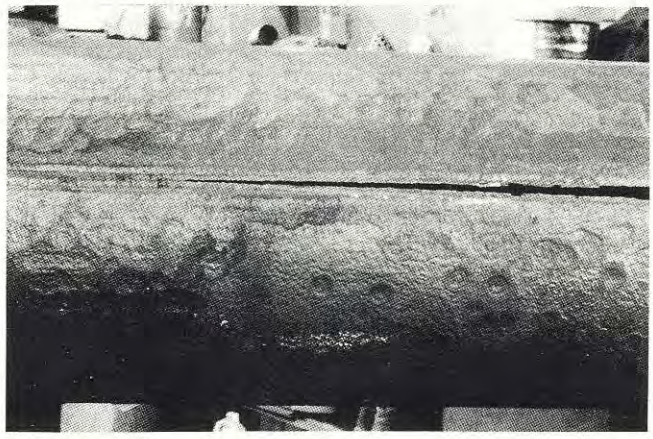

Fig. 14 Oxidized weld in rotary retort 1/4 X

The effect of Mo on oxidation depends upon levels of both Mo and Ni, the temperature, and whether the MoO_3 that forms accumulates or is removed by a free-flowing atmosphere. In Fig. 6 above, 3%Mo in the 45%Ni alloy N06333 did no apparent damage at extreme temperature in a gas-fired application. Under stagnant atmospheres, catastrophic oxidation is possible in this grade. [11] Catastrophic oxidation has been observed during creep-rupture tests of a 9%Mo 47Ni alloy at 1204°C (2200°F). [12] Higher nickel alloys are less sensitive to the detrimental effect of Mo. This may

be observed when annealing fabrications of the 6.2%Mo 24%Ni alloy N08367, welded with 8.5%Mo 61%Ni N06625. Any catastrophic oxidation that occurs will be on the 24% nickel portion. Taken to an extreme, Fig. 15 shows an N06625 weld bead lying between two completely oxidized plates of N08367, after the original weldment had been subject to 20 hours at 1093 °C (2000°F) in a box furnace.

Fig. 15

N06625 weld bead between scaled plates of N08367.

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