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PERFORMANCE OF HIGH TEMPERATURE ALLOYS IN A NATURAL GAS-FIRED COMBUSTION ENVIRONMENT

J. J. Barnes and S. K. Srivastava
Haynes International, Inc.
1020 W. Park Avenue
P. O. Box 9013
Kokomo, IN 46904-9013

ABSTRACT

The oxidation behavior of several Fe- and Ni-base commercial alloys, exposed in a slab/ingot reheating furnace for 46, 78 and 113 days, was studied. The furnace was fired by natural gas and operated at 2000-2250°F (1093-1232°C) with frequent cycles to 1000°F (538°C). Metal loss and internal penetration were measured and the mode of oxidation attack was examined using SEM/EDAX. It is shown that the alumina-forming 214 alloy suffered the least oxidation damage in the combustion environment. The chromia-forming alloys suffered metal loss, internal oxidation and void formation. The results of the field test are supported by laboratory oxidation data.

INTRODUCTION

Oxidation behavior is a primary consideration in selecting an alloy for service in a combustion environment. In this type of environment a protective oxide scale is essential to the survival of the alloy. An effective scale must be compact, slow-growing and chemically stable, but, most importantly, it must be able to withstand the stresses which develop during service. The stress which arises from thermal cycling is particularly damaging to oxide scales and commonly causes spalling of the scale. Continuous spalling leads to depletion in the protective oxide-forming element and breakaway oxidation takes place. This is characterized by deep internal oxidation and will severely limit the useful life of a component.

In addition to mechanical stability, an effective oxide scale must be chemically stable and slow-growing. Alumina scales are superior to chromia

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scales in these respects. Chromia is volatilized as CrO_3 at temperatures in excess of about 2000°F (1093°C) and chromia scales generally grow faster than alumina scales. The effectiveness of any scale is related to its healing ability, i.e., the ability to reform a protective barrier after failure of the scale. This ability depends on factors such as the composition of the alloy and the alloy interdiffusion coefficients.

The many factors which influence the oxidation behavior of an alloy at high temperatures under thermal cycling conditions were considered in assessing the performance of a range of commercial alloys exposed in a slab/ingot reheating furnace. In the furnace, which was fired by natural gas, coupons of the alloys were subjected to high temperatures (2000-2250°F, 1093-1232°C) and frequent thermal cycling to about 1000°F (538°C). The ability of the alloys to withstand these conditions was assessed through metallographic and electron optical examination of the exposed coupons. The results from the field test are compared with data from laboratory tests.

EXPERIMENTAL

The nominal chemical compositions of the alloys tested are listed in Table 1. Test racks consisting of coupons of the alloys were exposed in a slab/ingot reheating furnace for periods of 46, 78, and 113 days. The normal operating range of the furnace is 2000-2250°F (1093-1232°C) with regular cycles to about 1000°F (538°C).

After exposure, the alloy coupons were evaluated according to the procedure described in (1). Metal loss and depth of internal penetration were measured. The sum of these is referred to as maximum metal affected. Surfaces and cross-sections were examined by SEM and the corrosion product phases identified using EDAX.

RESULTS

The metal loss and maximum metal affected measurements for each exposure period are listed in Tables 2, 3 and 4. The alloys are ranked according to maximum metal affected. Some alloys suffered non-uniform attack and for these the metal loss measurements represent the area of deepest attack. Internal voids were a feature of most of the alloys and are included in the measurements of internal penetration.

The data show that 214™ alloy suffered the least oxidation damage in the combustion environment. In contrast, several of the stainless steels were completely consumed after only 46 days, and alloy 800H was completely consumed within 78 days. The measurements of maximum metal affected for the remaining alloys, i.e., 214 alloy, RA330®, alloy 600 and INCONEL® alloy 601, are plotted against exposure time in Figure 1, and the results of the analysis of the individual alloys are presented below. The plot shows the relatively low parabolic rate of oxidation of 214 alloy. Alloy 600 exhibited a linear increase in oxidation damage with time, whereas alloy 330 and alloy 601 obeyed a parabolic-type rate law. The scatter in the oxidation data is probably due to variations in furnace conditions with time.

The coupon of 214 alloy after an exposure of 113 days is shown in Figure 2. The alloy formed a uniform and adherent oxide scale. The scale is shown in cross-section in Figure 3 after an exposure period of 113 days. There was little

internal attack and the matrix was free of voids. An SEM/EDAX examination (Figure 4) revealed an inner layer of aluminum-rich oxide which was continuous and adherent beneath a layer rich in W, Co, Mo and Ca. These elements are apparently the result of contamination from the reheating furnace. Many of the alloys which are treated in the furnace contain W, Mo and Co; Ca may have originated from the furnace linings. The oxidation behavior of the alloy is not affected by these elements since the continuous oxide scale provides a barrier between the contaminants and the metal. An SEM examination of the scale surface confirmed the presence of Co-rich layers above a compact Al-rich layer. In some areas the outer layers had spalled but the protective alumina scale remained intact throughout.

Alloy 600 is a nickel-base alloy which forms a chromium-rich scale at high temperatures. The exposed coupon is shown in Figure 2. This alloy obviously suffered much more oxidation than 214 alloy and the scale had undergone extensive spalling. A cross-section of the alloy in Figure 3 shows the non-uniformity of the scale. There are areas of thick scale and areas of breakaway oxidation present. An SEM image of one of the breakaway areas is shown in Figure 5. Two layers were detected - an outer nickel-rich layer and an inner chromium-rich layer. Internal chromium-rich particles were found in the region of breakaway oxidation. This feature is evidently due to the failure of the external scale, probably as a result of thermal cycling.

The coupon of alloy 601 after an exposure of 113 days is shown in Figure 2. The alloy suffered extensive oxidation and scale spalling. The micrograph in Figure 3 shows extensive internal oxidation and void formation. These features are shown in detail in the SEM micrograph in Figure 6. The internal oxides close to the surface were found to be rich in chromium and the inner oxides were rich in aluminum. There was no external scale, which indicates that there was insufficient chromium present to form a protective layer. Consequently, chromium and aluminum were internally oxidized. This provides little protection against the environment.

Alloy 330 is an iron-base chromia-former which suffered extensive metal loss and void formation as a result of oxidation. The coupon which was exposed for 113 days in the combustion environment is shown in Figure 2. SEM images of the surface and cross-section are shown in Figure 7. The surface scale and EDAX analysis revealed the presence of several layers in the scale. The outermost layer was iron-rich and underlying layers were chromium-rich.

Silicon-rich areas were also detected and are shown in cross-section in the sub-scale region. Spalling of the external layer resulted in extensive oxidation of the alloy, primarily internal oxidation of silicon.

DISCUSSION

The field tests of alloys in the severe environment of the reheating furnace showed that 214 alloy is the most suitable material for these conditions. This conclusion is supported by the results of laboratory tests which were carried out under less severe conditions (2). The tests consisted of exposure for 1008 hours in flowing air at 1800, 2000, 2100 and 2200°F (982, 1093, 1149 and 1204°C). The results are listed in Table 5 and the data obtained at 2200°F are compared with the data from the 46-day (1104 hours) field test in Figure 8. The laboratory data shows that 214 alloy is consistently more oxidation-resistant than the other alloys at all temperatures in flowing air. It is clear from Figure 8 that the

field test was much more severe than the laboratory test, leading to greater oxidation damage in all of the alloys. The frequent thermal cycling in the field test was probably a principal factor in this difference. However, the alumina-forming alloy, 214 alloy, still performed significantly better than the other alloys.

The superior performance exhibited by 214 alloy in oxidizing environments is due to the formation of a tenacious, slow-growing and chemically stable scale. The 214 alloy exhibits the many advantages of alumina scale formers over chromia scale formers for elevated temperature/thermal cycling applications. Although alumina scales are inherently more brittle than chromia scales their properties are greatly improved by the presence of certain reactive elements (e.g. Y in 214 alloy). These reactive elements confer alumina scales with outstanding mechanical strength and adhesion. Thus, the scale on 214 alloy can withstand the stresses imposed by thermal cycling without spalling. Alumina is also very stable chemically at high temperatures.

It is evident that chromia scales did not offer sufficient protection to alloys under the combustion environment conditions. The degree of protection was found to vary greatly with alloy composition but in all cases the scale itself is unstable, volatilizing as CrO_3 at temperatures in excess of about 2000°F (1093°C). The iron-base alloys generally performed very poorly. All of the stainless steels, with the exception of alloy 330, were completely consumed within 113 days. The good oxidation behavior of alloy 330 is an illustration of the fact that increasing the amount of nickel in an iron-base alloy reduces the level of chromium necessary to form a continuous scale. The presence of silicon in that alloy may improve the scale stability but upon scale failure leads to a greater depth of internal oxidation. Alloy 800H which has a similar base composition to alloy 330 but a lower Si level performed poorly in the combustion environment.

The nickel-base chromia formers performed better than the iron-base alloys. Alloy 600 suffered much more metal loss than alloy 601, whereas 601 exhibited extensive internal attack, including void formation. Scale breakdown in alloy 601 resulted in extensive internal oxidation of aluminum.

Most of the alloys, including alloy 601 formed internal voids as a result of exposure in the combustion environment. This is an important factor since it will lead to a reduction in the strength of an alloy in service. Void formation is a direct consequence of oxidation. Vacancies produced by the oxidation process coalesce to form voids. In addition, voids may be produced by a Kirkendall effect, i.e., vacancies are created as a result of unequal fluxes of, for example, aluminum from the bulk alloy to the scale and nickel and chromium in the opposite direction for alumina-formers.[3] The vacancies thus produced coalesce to form voids. In chromia-forming alloys it has been established that voids occur in chromium-depleted zones (4). It is interesting to note that 214 alloy did not exhibit voids within the matrix after oxidation. This observation is consistent with the fact that, unlike chromia scales, alumina scales are formed by reaction at the oxide/metal interface. Thus, voids may only be created by a Kirkendall effect. The slow growth rate of the alumina scale on 214 alloy and its mechanical stability minimizes the outward flux of aluminum and the concomitant possibility of void formation.

CONCLUSIONS

1. The 214 alloy suffered the least oxidation damage in the combustion environment due to the strength and stability of the alumina scale.

2. The chromia-forming alloys suffered metal loss, internal oxidation and void formation due to scale breakdown under the thermal cycling conditions.

3. The nickel-base chromia-formers generally performed better than the iron-base chromia-formers. Increasing the nickel content reduces the amount of chromium necessary to form a protective scale.

4. All of the chromia-formers suffered void formation in the matrix.

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TABLE 1
NOMINAL CHEMICAL COMPOSITIONS OF THE ALLOYS TESTED
(Wt. %)

Alloy	C	Fe	Ni	Cr	Si	Mn	Others
Type 304 (UNS S30400)	0.08+	Bal	10.0	19.0	-	-	-
Type 310 (UNS S31000)	0.25+	Bal	20.0	25.0	-	-	-
Type 316 (UNS S31600)	0.08+	Bal	12.0	17.0	-	-	2.25Mo
RA330[49] alloy (UNS N08330)	0.05	43.0	35.0	19.0	1.25	1.5	-
Type 446 (UNS S44600)	0.20+	Bal	-	25.0	-	-	0.25N+
Alloy 800H (UNS N08810)	0.08	Bal	33.0	21.0	1.0+	1.5+	0.38Al, 0.38Ti
HAYNES® alloy No. 214	0.04	3.0	Bal	16.0	-	-	4.5Al, Y present
Alloy 600 (UNS N06600)	0.08+	8.0	Bal	16.0	0.5+	1.0+	0.35+Al, 0.3+Ti, 0.5+Cu
INCONEL[49] alloy 601(UNS N06601)	0.10+	14.1	Bal	23.0	0.5+	1.0+	1.35Al, 1.0+Cu

+ Maximum

[49] HAYNES is a registered trademark of Haynes International, Inc.
RA330 is a registered trademark of Rolled Alloys, Inc.
INCONEL is a registered trademark of the Inco Family of Companies

TABLE 2
OXIDATION DAMAGE FOR ALLOYS EXPOSED
FOR 46 DAYS IN THE REHEATING FURNACE

Alloy	Metal Loss μm (mils) per side	Maximum Metal Affected μm (mils) per side
214 Alloy	7.6 (0.3)	109.2 (4.3)
Alloy 600	368.3 (14.5)	520.7 (20.5)
Alloy 800H	482.7 (19.0)	635.1 (25.0)+*
Type 310	345.4 (13.6)	650.0 (25.6)+
Alloy 330	152.4 (6.0)	660.4 (26.0)+
Alloy 601	96.5 (3.8)	731.5 (28.8)+
Type 446	> 610.0 (24.0) consumed	consumed
Type 316	> 1397.0 (55.0) consumed	consumed
Type 304	> 1500.2 (63.0) consumed	consumed

Maximum metal affected = metal loss + maximum internal penetration

\+ voids present in matrix
* non-uniform attack

TABLE 3
OXIDATION DAMAGE FOR ALLOYS EXPOSED
FOR 78 DAYS IN THE REHEATING FURNACE

Alloy	Metal Loss μm (mils) per side	Maximum Metal Affected μm (mils) per side
214 alloy	10.2 (0.4)	10.2 (0.4)
Alloy 330	426.7 (16.8)	642.6 (25.3)+
Alloy 600	655.3 (25.8)	807.7 (31.8)+
Alloy 601	170.2 (6.7)	932.2 (36.7)+
Alloy 800H	> 762 (20.0) consumed	consumed

Maximum metal affected = metal loss + maximum internal penetration

\+ voids present in matrix

TABLE 4
OXIDATION DAMAGE FOR ALLOYS EXPOSED
FOR 113 DAYS IN THE REHEATING FURNACE

Alloy	Metal Loss μm (mils) per side	Maximum Metal Affected μm (mils) per side
214 alloy	12.7 (0.5)	114.3 (4.5)
Alloy 330	393.7 (15.5)	647.7 (25.5)+
Alloy 601	182.9 (7.2)	944.9 (37.2)+
Alloy 600	635.0 (25.0)	1143.0 (45.0)+*
Alloy 800H	> 787.4 (31.0) consumed	consumed
Type 446	> 610.0 (24.0) consumed	consumed
Type 310	> 1041.4 (41.0) consumed	consumed
Type 304	> 1524.0 (60.0) consumed	consumed
Type 316	> 1600.2 (63.0) consumed	consumed

Maximum metal affected = metal loss + maximum internal penetration

\+ voids present in matrix
* non-uniform attack

TABLE 5
OXIDATION DATA FOR ALLOYS EXPOSED IN FLOWING AIR FOR 1008 HOURS AT VARIOUS TEMPERATURES

Alloy	Metal Loss + Internal Penetration, μm (mils) per side			
	1800°F (982°C)	2000°F (1093°C)	2100°F (1149°C)	2200°F (1204°C)
214 alloy	5 (0.2)	3 (0.1)	8 (0.3)	18 (0.7)
Alloy 600	23 (0.9)	41 (1.6)	74 (2.9)	213 (8.4)
Type 310	28 (1.1)	58 (2.3)	112 (4.4)	262 (10.3)
Alloy 601	46 (1.8)	97 (3.8)	196 (7.7)	302 (11.9)
Alloy 800H	46 (1.8)	188 (7.4)	226 (8.9)	345 (13.6)
Type 446	58 (2.3)	368 (14.5)	> 584 (23.0)	(1000h)[1]
RA 330	109 (4.3)	170 (6.7)	221 (8.7)	211 (8.3)
Type 304	206 (8.1)	> 584 (23.0)	> 584 (23.0)	(336h)[1]
Type 316	363 (14.3)	> 1753 (69.0)	> 2642 (104.0)	(168h)[1]

[1] alloy consumed in test

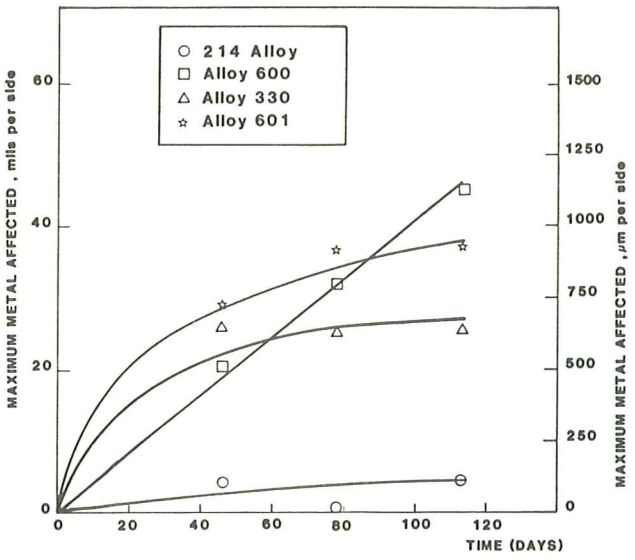


FIGURE 1 - Oxidation data for alloys exposed in the reheating furnace

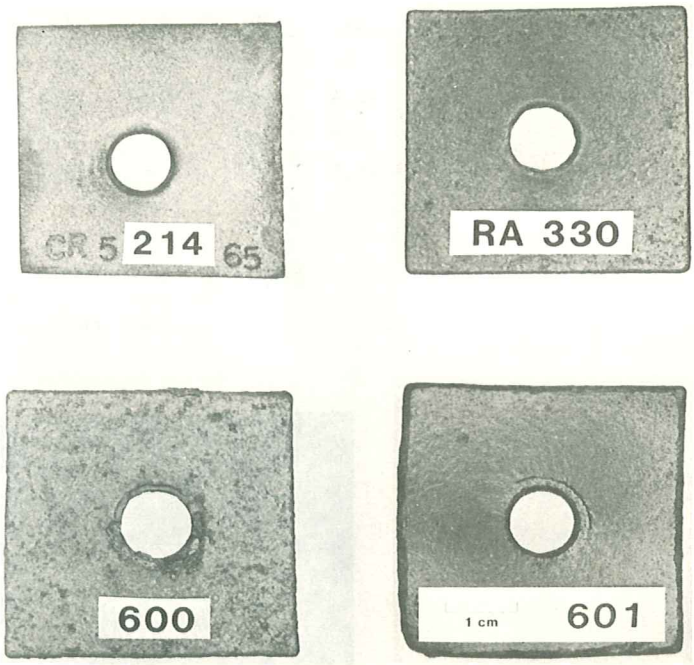


FIGURE 2 - Photographs showing appearance of coupons after 113-day exposure in the reheating furnace

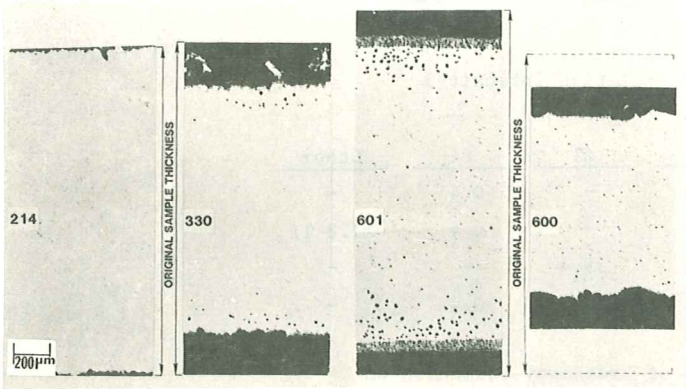
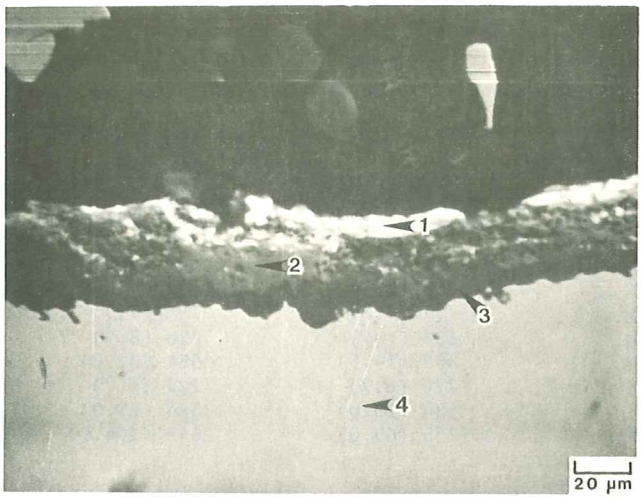


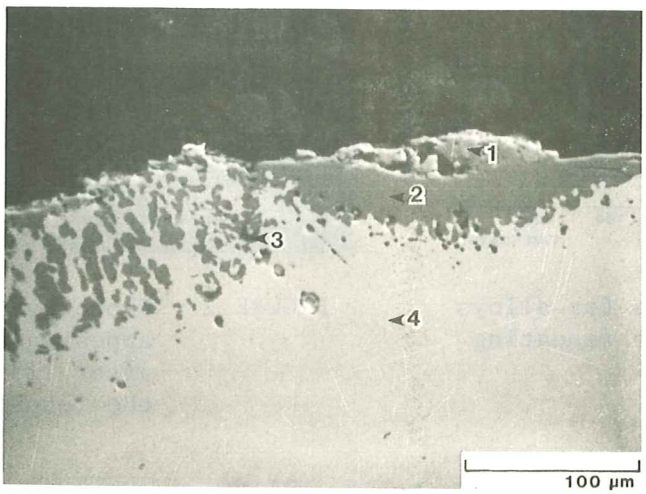
FIGURE 3 - Photomicrographs showing comparative degree of attack after 113-day exposure in the reheating furnace; as polished (from Ref. 5)



Semi-Quantitative Analysis (Relative Intensity)

Area	Cr	Fe	Co	Ni	Al	Ca	Zr	Mo	W
1	-	-	-	-	-	35.2	-	11.0	53.8
2	12.4	1.2	13.8	37.1	34.5	1.0	-	-	-
3	1.5	0.7	0.2	1.7	89.6	4.7	1.7	-	-
4	29.5	2.2	-	67.4	0.9	-	-	-	-

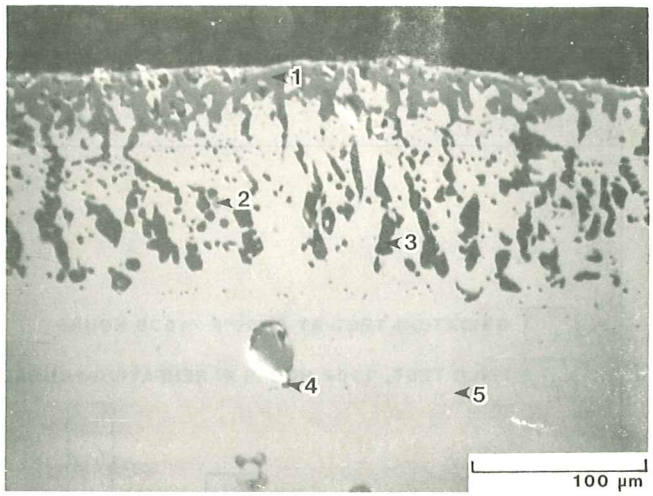
Figure 4: SEM/EDAX of cross-section of 214 alloy after 113-day exposure; note the thin aluminum-rich scale.



Semi-Quantitative Analysis (Relative Intensity)

	Cr	Ni	Fe	Mn	Al	Si	Other
1	18.3	74.0	7.1	-	-	0.4	-
2	97.2	0.4	0.2	-	-	0.4	1.8 Ti
3	51.6	7.6	1.5	-	39.4	-	-
4	17.3	73.4	9.2	-	-	0.1	-

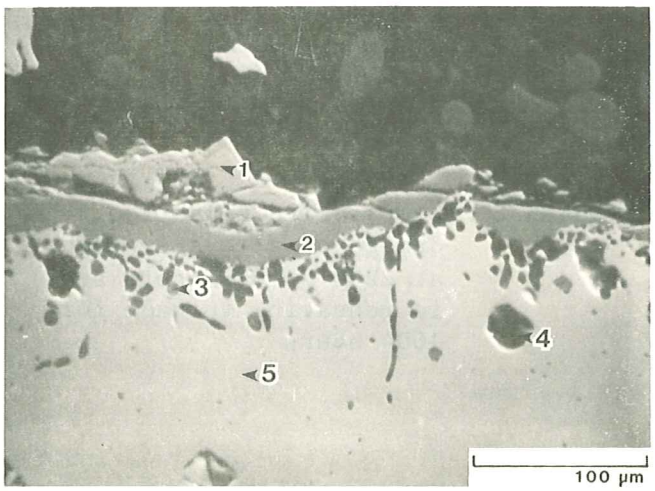
Figure 5: SEM/EDAX of an area of breakaway oxidation on alloy 600 after 113-day exposure



Semi-Quantitative Analysis (Relative Intensity)

Area	Cr	Fe	Ni	Al	Ti	Other
1	92.0	0.1	0.5	2.2	5.2	-
2	12.6	21.7	57.3	8.2	-	0.15
3	6.0	7.2	17.9	68.1	-	0.95
4	16.9	18.6	51.8	-	0.5	11.1 Mg
5	20.4	18.8	60.7	-	-	0.1 Si

Figure 6: SEM/EDAX of an area of breakaway oxidation on alloy 601 after 113-day exposure



Semi-Quantitative Analysis (Relative Intensity)

Area	Cr	Fe	Ni	Si	Other
1	7.1	6.7	76.6	-	9.5 Mn
2	98.9	0.2	-	0.3	-
3	74.6	7.1	3.9	-	13.9 Ti
4	8.4	23.2	10.5	57.6	-
5	25.2	27.0	47.3	0.5	-

Figure 7: SEM/EDAX of cross-section of alloy 330 after 113-day exposure

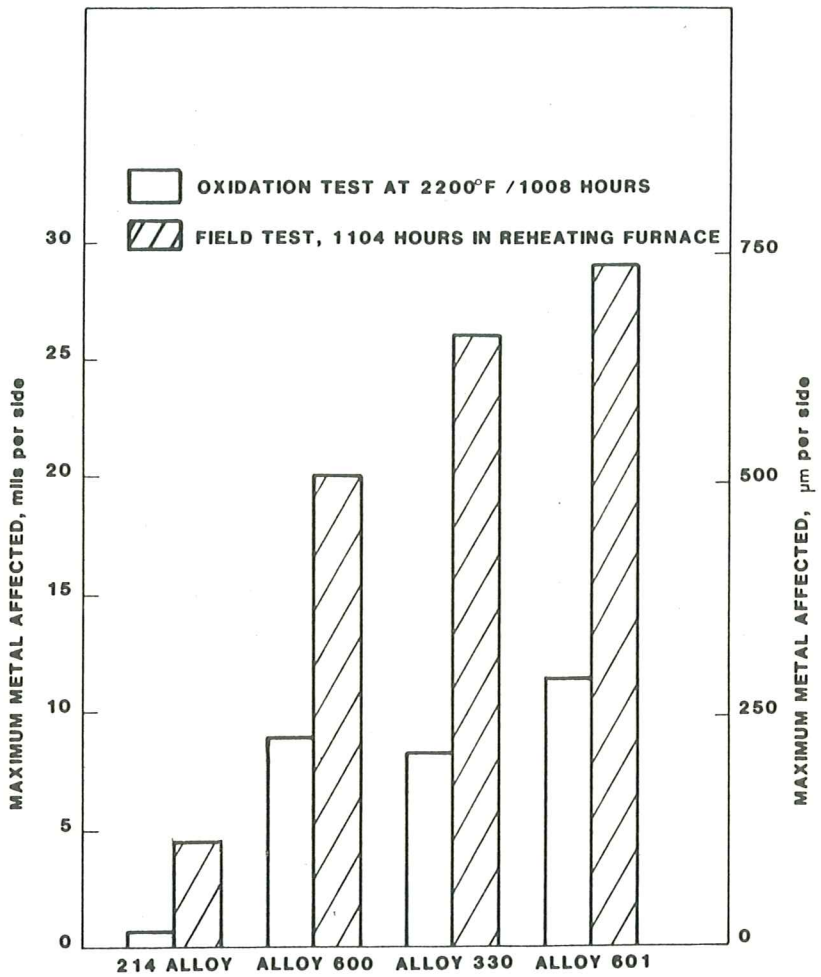


FIGURE 8 - Comparative oxidation damage of alloys exposed at 2200°F/1008 hours and in reheating furnace for 1004 hours