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EVALUATION OF HEAT RESISTANT ALLOYS IN COMPOSITE FIXTURES

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ABSTRACT

The deterioration of heat resistant alloys is often due to absorption of carbon in carbonaceous environments. Rapid heating or cooling may contribute to the effects of carburization. These effects are difficult to assess from coupon exposure alone or from laboratory tests. The approach of this paper is to evaluate damage in service from composite fixtures, those containing a number of heat resistant alloys as individual components of the same fixture. Bar frame baskets and retaining fixtures used in atmospheres containing carbon provide comparative field data on the amount of carburization. The use of bar baskets in quenching service also provides comparative field data on fatigue damage. Nine austenitic Fe-Cr-Ni alloys varying in nickel from 11 to 61 percent have been examined after 15 months service in a bar frame basket. Carburization, thermal fatigue, and selective oxidation of carbides contribute to deterioration. Carburization in this service is compared to a laboratory test conducted in a commercial compound of "activated" coke. Thermal fatigue, evident as intergranular micro voids, is conspicuous in several alloys. Tensile tests of damaged material is compared to the original material as a measure of the severity of fatigue damage.

INTRODUCTION

The most common materials used for heat resistance above 1400°F (760°C) are austenitic alloys containing iron, chromium, and nickel as major elements. These include T304 (UNS No. S30400) at the low range of nickel and Inconel 600 (UNS No. N06600) at the high range. They usually contain chromium from 17 to 27 percent and are commonly modified to improve their resistance to carburization and oxidation. Solution strengthened grades are available for high temperature strength.

The use of heat resistant materials is often limited by absorption and diffusion of carbon; in fact, this is the most common source of unexpected failure judging from documented failure investigations over a period of twenty-five years. Damage from the effects of rapid heating and cooling over an extended number of thermal cycles is a second common source of failure. This damage is often aggravated by carburization. The interacting effect of both in welded structures is difficult to predict from laboratory data alone.

FIELD EVALUATION OF COMPOSITE FIXTURES

Ideally service data reflect the combination of hot corrosion, mechanical loading, and thermal cycling that corrosion test racks cannot simulate. To be most useful this approach should not be limited to one test site and may be supplemented with coupon exposure in the field in addition to laboratory tests.

This approach has been used for two and a half years involving a wide range of iron-chromium-nickel heat resistant alloys. Bar frame baskets and retaining fixtures subjected to carburizing and quenching for extended exposure, provide the service data to be presented in this paper. A bar frame basket removed after 15 months in heat treating service is shown in Figure 1. The basket is constructed from 1/2 inch (13 mm) diameter bar and requires a large number of welds. Seven commercial and two developmental heat resistant alloys were used as individual components of the bar basket. The advantage of exposing nine materials in one basket is that service variables are reduced from one component to another.

MATERIALS AND PROCEDURE

The alloys included in 15 month service are listed in Table 1 with the nominal composition. These materials vary in nickel from 11 to 61 percent. Elements added to enhance hot corrosion or strength are indicated in Table 1.

Service conditions include rapid thermal cycling in carbonaceous atmospheres used for carburizing, carbonitriding and neutral hardening. These atmospheres are provided from a base of endothermic gas containing 40 percent nitrogen, 40 percent hydrogen, 20 percent carbon monoxide. This base is enriched with natural gas and ammonia depending on the specific application. Service temperature varied from 1550 to 1700°F (840 to 930°C). The baskets were oil quenched from 1550°F (840°C).

Full cross sections of each alloy bar in the composite bar basket were prepared for metallographic examination. These are examined and photographed at reduced magnification to reveal the depth and uniformity of carburization. Surface cracking and internal damage are also evident from photomacrographs (Figures 2 through 6).

The depth of carburization was measured by metallographic observation, using the image of the carburized layer on the focusing plate of a metallograph. This may be measured at different magnifications depending on the depth of carburization. Most data were based on observation at 100 or 200x magnification. Different magnifications for the same sample are useful for verifying case depth measurement. The amount of carbon absorbed at the surface, and the variation of carbon with distance from the surface have been determined by chemical analysis f machined layers. Chemical analysis of these layers also indicates the approximate depth of carburization. In addition to measuring the depth of carburization, the same metallographic cross sections are examined to determine the effect of carburization on surface integrity.

Metallographic cross sections also indicate that severe internal damage occurred in several alloys. To some extent this damage was observed in all of the components of the bar basket. This is evident as grain boundary micro voids near the center of the bar. The presence of grain boundary voids would be expected to reduce the mechanical properties. Therefore, room temperature tensile data were obtained for each alloy in the damaged condition. Tensile tests of the same lots of each alloy were performed in the unexposed condition. The ratio of exposed to unexposed tensile properties provides a quantitative expression for fatigue damage. In these tests the gauge diameter of .250 inches (6.4 mm) was sufficient to remove the carburized layer from the gauge portion of the tensile specimen.

Grain size determinations of each alloy in the original condition were performed using a circular intercept method described in ASTM E 112-80. The 95% confidence limits may be determined using the circular intercept method. This was typically $\pm$ .3 of an ASTM grain size number, i.e. ASTM 7.2 $\pm$ .3.

Laboratory carburization tests have been used to evaluate heat resistant alloys. These are typically performed at 1800°F (980°C) for 15 days. The test has been used over a period of four years for a variety of materials, including materials exposed in the test site of this paper. The laboratory test is based on heating carburization test bars in a box containing a commercial carburizing material.(1) The specimens are given a uniform surface treatment by centerless grinding to a common diameter of .450 inches (11 mm). Evaluation is based on carbon analysis of machined layers, and measurement of carbon penetration. An advantage of using specimens having a cross section of this approximate size, is that one may determine the carbon gradient and case depth. Carburization testing of thin coupons, less than 3/16 inches thick (4.7 mm), at this temperature and time will result in complete penetration of the cross section. The use of specimens that carburize through the cross section may simulate service conditions for sheet, however it does not apply equally well for heavier plate or bar.

RESULTS OF FIELD EXPOSURE-CARBURIZATION

Metallographic cross sections of all nine alloys reveal the depth and uniformity of carburization. In general the depth of carburization decreases in order of increasing nickel content. Five alloys are shown in the photomacrographs of Figures 2 through 6 as an illustration of iron base, iron-nickel, and nickel alloys. Of these five, RA 253MA (UNS S30815) has the lowest nickel content. It is shown in Figure 2 at a magnification of 5x. This alloy carburizes quite uniformly to a depth of 90 mils (2300 μmm). Carburization of this alloy is shown in the macrograph as a grey area extending in from the surface of the 1/2 inch (13 mm) round bar. The presence of a crack extending to the depth of the case serves as an indicator of case depth in this macrograph. Incoloy 800 (UNS N08800) is shown in a similar cross section in Figure 3. Carburization of this 31Ni-19Cr alloy is non-uniform showing two marked carburized areas in the same quadrant of the cross section as the deep surface crack. The surface crack is carburized around the root of the crack, indicated by white under oblique illumination. Maximum case depth is 50 mils (1300 μmm) at the area shown near the upper right corner of Figure 3. An alloy containing 36Ni-18Cr-2Si-Bal.Fe (Alloy BSC) is shown in Figure 4. In spite of the addition of silicon for carburization resistance, this alloy has carburized uniformly to a depth of 70 mils (1800 μmm). This alloy was provided by the supplier in a uniformly medium coarse grain size, ASTM 3.6. Associated with the coarse grain size is a series of surface intergranular cracks around the periphery of the cross section and extending through the carburized surface. Several of the deepest cracks have carburized severely on the crack surface and appear white in the macrograph of Figure 4. These are convenient markers of case depth.

RA 333 (N06333) containing 45 percent nickel with 1% silicon for carburization resistance is shown in Figure 5. The carburized surface is relatively shallow and non-uniform at 20 mils (500 μmm) maximum depth.

Inconel 601 (N06601) containing 61 percent nickel with an addition of 1 percent aluminum is shown in Figure 6. The carburized layer is relatively shallow at 20 mils (500 μmm) and uniform. Inconel 601 was provided with a grain size of ASTM 4.0, and as for alloy BSC, has developed a series of intergranular surface cracks extending to the depth of the case.

The depth of carburization from metallographic measurement and the amount of carbon absorbed in service are summarized in Table 2 for nine

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(1) Park Chemical Company 'NB Special'

alloys. Iron base alloys characterized by 21Cr-11Ni-1.7Si developed the deepest case and highest carbon content, 90 mil depth (2300 μmm). Alloys containing 31 to 36% Ni have case depths varying from 50 to 80 mils (1300 to 2000 μmm). In these alloys the effect of silicon is masked by grain size. Two iron base alloys in Table 2 display significant difference in resistance to carburization as measured by surface carbon. RA 85H has absorbed less than two thirds the amount of S30815. This is due largely to silicon, although finer grain size may also contribute. Three alloys containing 45 to 61 percent nickel have case depths about one third that of 35 Ni alloys.

RANKING OF CARBURIZATION RESISTANCE IN LABORATORY PACK CARBURIZING TESTS

The choice of the most realistic laboratory carburization test is one in which there may be considerable disagreement. Pack carburizing tests have been used for many years and are considered here as a useful screening test. In terms of surface carbon and case depth, pack carburizing at 1800°F (980°C) is more severe than field exposure in this test site.

A pack carburizing test in which ten commercial alloys were included in the same box indicates that carburization resistance increases with nickel content from S30400 to N06601. The carburized case was found to vary from 40 mils (1000 μmm) for N06333 to greater than 225 mils (5700 μmm) for S30400. This general relationship is indicated in Figure 7. Considering the lack of precision in identifying the boundary of carburized material for Fe-Cr-Ni austenitic allloys, the agreement shown in Figure 7 is reasonable. These data are in agreement with data for cast Fe-Cr-Ni alloys of varying nickel content.[1] In two particular test sites containing the alloys of Table 1, laboratory pack carburizing tests agree with service data. The relationship of laboratory data to field data is illustrated in Figure 8, using 15 month service data (Table 2) against 15 day pack carburizing data. It seems likely that no laboratory evaluation based on unstressed bars or coupons will reflect grain size differences among materials. Thus alloys BSC and N08800 having large grain size variation, and different service case depth are identical in laboratory testing. This is also evident upon observing the clustering of data for 35 percent nickel alloys in Figure 7 (pack carburizing) and separation of data points for the same alloys in Figure 8 (service carburizing).

RESULTS OF FIELD EXPOSURE INTERNAL FATIGUE

Internal damage to various alloys may be observed from polished cross sections at reduced magnification. In Figure 4 of BSC (36Ni-18Cr-2Si-Bal.Fe) this internal damage is evident as white - irregular markings in the central area of the transverse section of the bar. At higher magnification these irregular markings are more obvious as intergranular voids. This is most evident in Figure 4, however, it is severe enough to observe in several alloy components at reduced magnification. This is shown in Figures 2 (S30815) and 6 (N06601).

In order to rate nine alloys more objectively, the effect of intergranular micro voids on mechanical properties was determined. Ordinary tensile tests at room temperature were performed on the bars in the damaged condition. The worst cases of internal damage were reflected in drastic loss of tensile strength. Alloy BSC retained a tensile strength of only 27,300 psi (188 MPa) compared to 84,200 psi (580 MPa) in the unused condition. The ratio of used to unused tensile strength is .32. This ratio is an expression of the retention of mechanical properties and will be applied in comparisons to follow. Alloy N06601 retains about two thirds (.69) of its tensile strength. This ratio exceeded .9 for three alloys, all of which were placed in service with a fine grain size, ASTM grain size number 7 or greater.

Tensile ductility was found to be even more drastically reduced by thermal fatigue and has been summarized in Table 3 for nine materials having a range of grain size as shown. Austenitic alloys have characteristically high tensile ductility and for these alloys the original tensile ductility has been omitted for brevity. Tensile ductility in the used condition varied from 0.7% for BSC to 68.2% for N08800. Expressed as the ratio of final to original, tensile ductility ratios were .01 for BSC to 1.06 for N08800. Both final ductility, and the ratio of final to original ductility are given in Table 3.

A comparison of retention of ductility to original grain size suggests that grain size is an important factor in degradation of properties by fatigue. This factor has been recognized for 20 years in the application of alloys for heat treating service involving oil quenching. Alloy N08330 is provided with grain size of ASTM number 5 or greater for this reason. Two low nickel alloys (11 and 14%) shown in Table 3 retain less ductility than 35 percent nickel alloys of similar grain size. Considering the difference of thermal expansion for 11% and 35% nickel alloys, it is not surprising that lower nickel alloys are more affected by fatigue damage.

ROLE OF CREEP AND FATIGUE IN HIGH TEMPERATURE SERVICE INVOLVING RAPID HEATING OR COOLING

Austenitic alloys have highest creep properties when they are solution heat treated to relatively coarse grain sizes such as ASTM grain size number 5 or less.[2] As an example N08330 has values of 2000 psi (13.8 MPa)(2) as annealed to a grain size of ASTM 7 and 2800 psi (19.3 MPa) when annealed to ASTM 5. The viewpoint of this paper is that intergranular micro voids as illustrated, are the result of fatigue rather than creep. The stress involved in fatigue damage is differential thermal contraction between the surface and center of bar components during quenching. The data in Table 3 indicate that fine grain size is desirable to reduce damage. Since this is opposed to the direction for best creep-strength, it appears that damage occurs by fatigue rather than creep. It has been generally observed that internal damage increases with section size.[3] This cannot be accounted for by a damage-process involving creep (as commonly measured in constant load - isothermal tests). Further, it was found that alloy components showing severe loss of tensile strength showed no unusual deformation in service. These components would presumably have markedly less creep resistance.

EFFECT OF CARBURIZATION

Photomacrographs in Figures 2 through 6 and data in Table 2 provide means for measuring the extent of carburization without clarifying the effect on service life. Carbon combines with chromium to form chromium carbide in Fe-Cr-Ni alloys. The presence of surface carbon as high as two percent results in most of this as carbide, forming on grain boundaries and twin boundaries. This results in severe embrittlement. Bending ½ inch (13 mm) carburized bars through an angle of 45° resulted in deep surface cracking of BSC and N08330. Alloys Incoloy DS (35Ni-17Cr-2.4Si) and N08800 were bent 90° with less severe cracking. Nickel-base alloys are the most ductile accepting 90° bends with only superficial cracking. Alloy S30815 containing 11 percent nickel cracked most deeply when cold bent 10°.

In addition to loss of mechanical properties, carburization results in potential degradation by grain boundary oxidation. This selective oxidation along the interface of chromium carbides and the matrix is analogous to sensitization of stainless steels. The most obvious analogy is that of chromium depletion.

It has been shown that HK40 (26Cr-20Ni) becomes magnetic upon carburization.[4] Measurements of magnetic permeability and chromium content in the matrix demonstrate that a large increase in permeability occurs when the matrix chromium is less than 15 percent. In the case of carburized HK40, chromium content in the matrix was reduced to 5 percent. Wrought heat resistant alloys, most notably N08330 become strongly magnetic as a result of carburization. This simple test has been used for field inspection for many years.

(2) Stress to produce 1% creep in 10,000 h at 1600°F (870°C).

Chromium depletion along carbides is also suggested from metallographic examination in the present work. Grain boundaries and twin boundaries of surface grains are filled with oxide. Subsurface grain boundary carbides are incompletely oxidized, with the carbides typically being outlined by oxide. This zone may be about 25 mils (650 μmm) deep, and terminates at unaffected carbides within the carburized layer.

Selective oxidation is shown in Figure 9 for alloy N08330. This mechanism is closely linked with the growth of surface cracks illustrated for five alloys in Figures 2 through 6. Surface cracks are oxidized intergranular cracks that vary in depth with the depth of carburization and that vary in frequency with grain size. The alloy of coarsest grain size, BSC developed surface cracks at most of the intersections of grain boundaries with the surface of the bar. This alloy has failed within six months in a test site involving carbonitriding.

It has been observed that a wide range of Fe-Cr-Ni alloys including those in Table 1 become magnetic in highly carburizing conditions. However, it is misleading to assume that alloys may always be inspected with a magnet to assess carburization regardless of the carburizing conditions. The reason for this is clear from the work of Rees et al.[5] In investigating the constitution of Fe-Cr-Ni alloys the authors identified 66 alloys in the system as magnetic or nonmagnetic. When this property is located on ternary coordinates, an irregular boundary, dividing magnetic alloys is constructed. This boundary is close to some alloys (19Cr-35Ni) and well separated from others (25Cr-20Ni). Chromium depletion from carburization must be severe enough to produce a large change in chromium in depleted areas of 25Cr-20Ni alloys. In alloys such as N08330 the composition is so close to magnetic alloys that any small change in surface composition will produce the same effect as carburization. This includes formation of chromium oxide on the surface of specimens oxidized at 2000°F (1090°C).

Diffusion of chromium into a depleted area has been observed for carburized S30815 (21Cr-11Ni). Initial exposure for 15 months resulted in a nonmagnetic alloy becoming strongly magnetic. When this was heated to 1800°F (980°C) for 24 hours, the sample again became nonmagnetic.

Machined layers, well below the surface of carburized specimens, are magnetic for sensitive alloys such as N08330.

STRAIN INDUCED GRAIN COARSENING

Unusual grain coarsening effects may be noted in materials exposed to rapid cooling or heating. In a number of instances involving different test sites and different alloys, coarse grain areas are evident. In the present examination of N08800, grain coarsening occurred near the root of the deep surface crack shown in Figure 3. Grain coarsening also was observed in the center. Grain coarsening in both areas is shown in Figure 10.

Austenitic Fe-Cr-Ni alloys exhibit strain-sensitive recrystallization upon cold working at ambient temperature and reheating to 1800°F (980°C). This effect is similar to that shown in Figure 10.

SUMMARY

Carburization resistance of nine Fe-Cr-Ni alloys containing nickel from 11 to 61 percent has been evaluated in field exposure at 1550° to 1700°F (840°C to 930°C) for 15 months. All of the alloys were provided as individual components of a bar frame basket, used for a combination of carburizing, carbonitriding and neutral hardening, followed by oil quenching from 1550°F (840°C).

The depth of carburization varied from 90 mils (2300 μmm) for an 11 percent nickel alloy to 20 mils (580 μmm) for two nickel base alloys. Four alloys containing a nominal nickel content of 34 percent and similar chromium, vary from 50 mils (1300 μmm) to 80 mils (2000 μmm). The best of these four alloys was provided to the finest grain size, ASTM No. 10.8. Next in order of decreasing resistance in this group was an alloy modified with 2.4 percent silicon, but with a grain size coarser by 3.5 grain size numbers. No clear effect of silicon content in these four alloys is apparent. This is attributed to grain size variation within the group. The coarsest grain alloy contained numerous intergranular surface cracks in the case. The addition of silicon in low nickel alloys (11 to 14 percent) is beneficial, up to at least 3 percent silicon in RA 85H. This alloy has similar carburization resistance to much higher nickel alloys, notably N08330.

Oil quenching in this test site resulted in severe loss of mechanical properties as determined from ordinary tensile tests. In terms of tensile ductility, an alloy with grain size of ASTM 3.6 had nil ductility after service. In two other alloys ductility was drastically reduced. Nickel base alloys are more resistant to this damage than iron base alloys of similar grain size. Repeated quenching and reheating is responsible for this condition (thermal fatigue). Within each of the three groups of alloys (12%, 34%, and 46% nominal nickel) resistance to fatigue damage correlates with grain size. The most resistant alloys have the finest grain size.

Laboratory pack carburizing tests at 1800°F (980°C) for 15 days correlate well with field exposure. Because laboratory tests do not involve rapid thermal cycling, they do not reflect grain size effects noted in field evaluation.

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TABLE 1

Composition of Alloys Exposed in Service, Weight Percent

Alloy UNS No. or Trade Name	Ni	Cr	Fe (By Diff.)	Other Si	Al	Ce	W	Mo	Co	N
				Hot Corrosion			Strength			
S30815	11	21	65	1.7	-	.06	-	-	-	.17
RA 85H	14	18	63	3	1	-	-	-	-	-
N08800	31	20	48	-	-	-	-	-	-	-
N08330	35	19	45	1.2	-	-	-	-	-	-
Incoloy DS	35	17	45	2.4	-	-	-	-	-	-
BSC	36	18	43	2.0	-	-	-	-	-	-
XK4	45	25	<20	2	-	-	-	-	-	-
N06333	46	25	18	1	-	-	3	3	3	-
N06601	61	23	15	-	1.3	-	-	-	-	-

TABLE 2

Carburization of Alloys Exposed 15 Months

Alloy UNS No. or Trade Name	Original Grain Size, ASTM No.	Depth of Carburization Mils (µmm)	Absorbed Carbon, % in .06 inch (1.5 mm) Surface Layer
S30815	6.4	90 (2300)	1.19
RA 85H	11.3	80 (2000)	.70 - .79 *
N08800	10.8	50 (1300)	.14
N08330	4.6	80 (2000)	.34 - .75 *
Incoloy DS	7.2	60 (1500)	.25
BSC	3.6	70 (1800)	.54
XK4	6.9	30 (660)	.09
N06333	7.1	20 (580)	.15
N06601	4.0	20 (580)	.10

*Duplicate components were included in the bar frame basket.

TABLE 3

Retention of Tensile Ductility in Service

Alloy UNS No. or Trade Name	Tensile Ductility After Service, % Reduction of Area	Ratio, Final Ductility / Original Ductility	Original Grain Size, ASTM Grain Size No.
S30815	19.3	.28	6.4
RA 85H	28.4	.46	11.3
N08800	68.2	1.06	10.8
N08330	45.6	.62	4.6
Incoloy DS	40.6	.63	7.2
BSC	.7	.01	3.6
XK4	51.3	.77	6.9
N06333	51.8	.77	7.1
N06601	19.3	.28	4.0

Figure 1
Composite fixture containing nine alloys. In service 15 months.

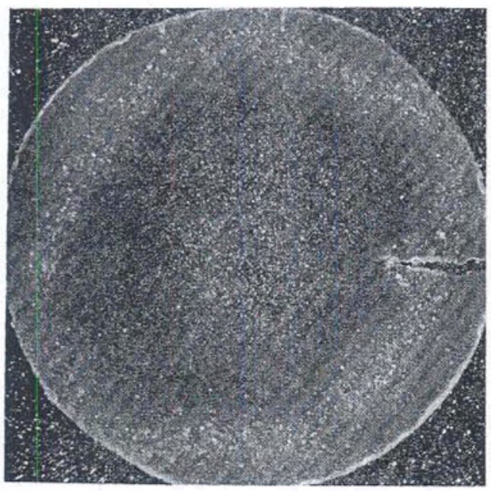

Figure 2
Alloy S30815 (21Cr-11Ni). 5x

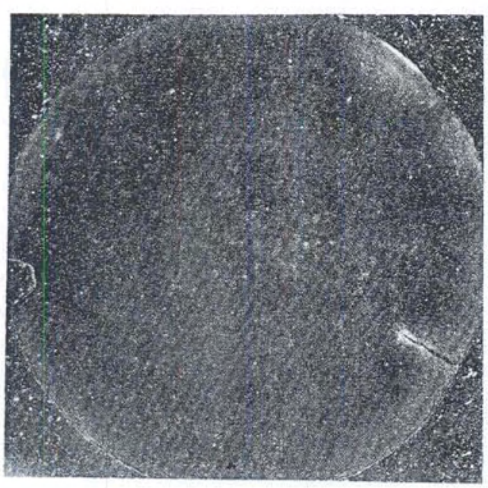

Figure 3
Alloy N08800 (20Cr-31Ni). 5x

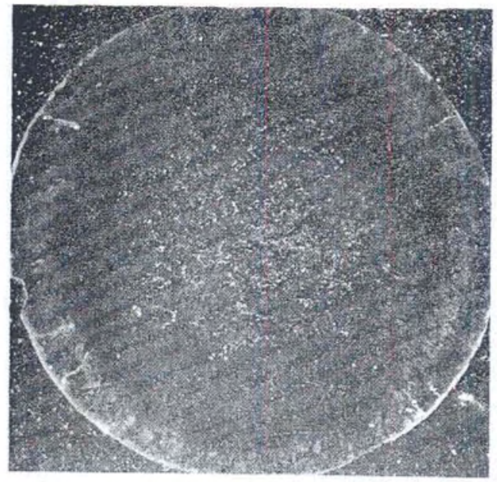

Figure 4
Alloy BSC (18Cr-36Ni-2Si). 5x
Grain Size ASTM 3.6

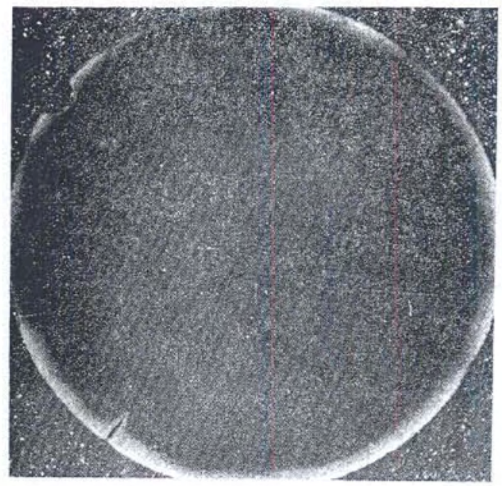

Figure 5
Alloy N06333 (25Cr-46Ni-1Si). 5x

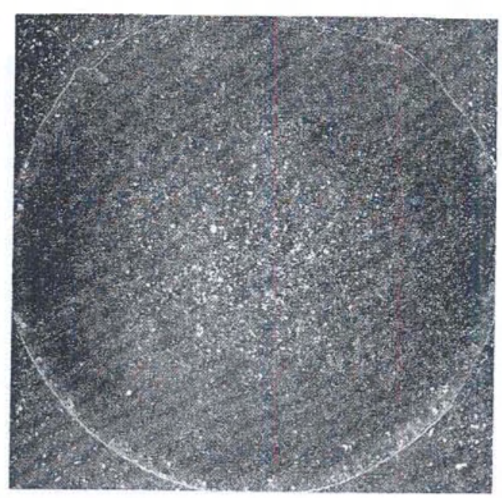

Figure 6
Alloy N06601 (23Cr-61Ni). 5x

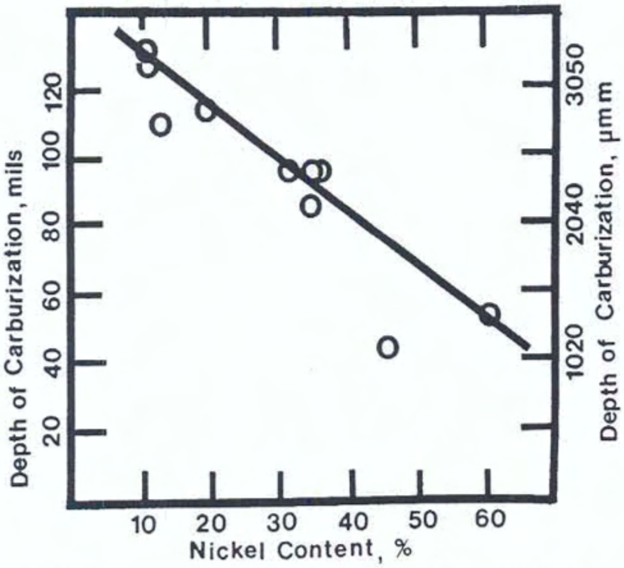

Figure 7— Effect of Nickel on Carburization

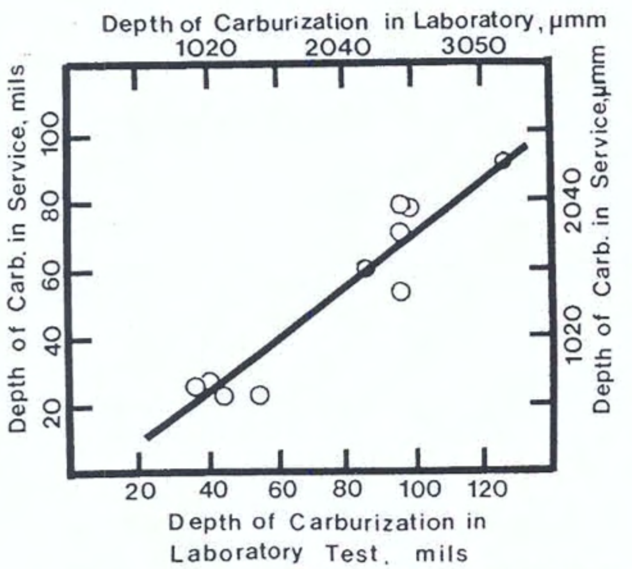

Figure 8— Service Data vs. Laboratory Data.

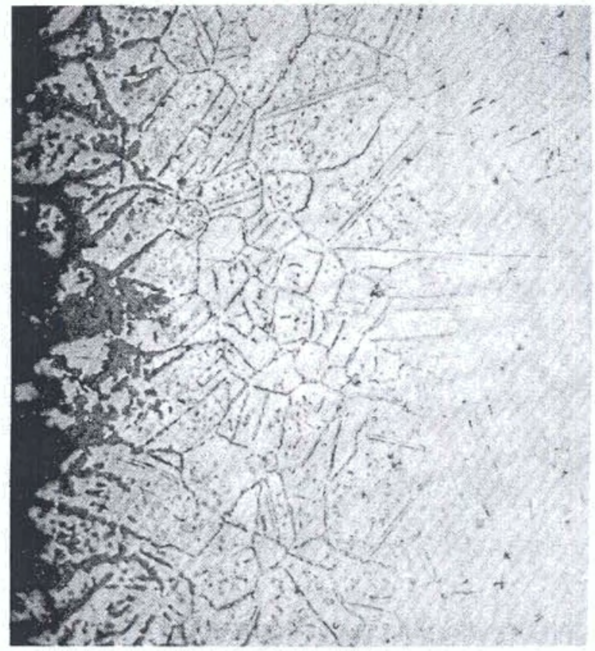

Figure 9
Surface of N08330 bar used in austempering fixture for 10 months. Intergranular oxidation at the left occurs by selective oxidation of carbides. This process is shown at several stages going from the surface at the left to unoxidized carbides at the extreme right. Magnification - 100x

Figure 10
Cross section of N08800 shown in Fig. 3. Grain coarsening occurs in an area extending outward from the tip of the crack and upwards approximately half the vertical direction of the field of view. The extreme center of the bar along the top edge is also grain coarsened in service. Magnification - 15x