

HAYNES
International

Haynes International, Inc.
1020 West Park Avenue
P.O. Box 9013
Kokomo, Indiana 46902-9013
317-458-6000

To: Library (10)

Date: May 9, 1991

Subject: "A New High Strength Fe-Ni-
Cr-Nb-N Alloy for Elevated
Temperature Applications"

From: S. C. Ernst

Project: 816-10005

File: 13314

Copies: J. J. Barnes G. Y. Lai
 D. E. Fluck R. J. Myers
 F. G. Hodge C. J. Sponaugle
 D. L. Klarstrom S. K. Srivastava
 H. J. Klein File

Attached is a copy of a paper entitled "A New High Strength Fe-Ni-Cr-Nb-N Alloy for Elevated Temperature Applications", which I will present at the First International Conference on Heat-Resistant Materials, 22-26 September 1991, at Lake Geneva, Wisconsin.


S. C. Ernst

A NEW HIGH STRENGTH Fe-Ni-Cr-Nb-N Alloy FOR ELEVATED TEMPERATURE APPLICATIONS

S.C. Ernst and G. Y. Lai

ABSTRACT

A new nitrogen strengthened Fe-Ni-Cr alloy has been developed for elevated temperature applications. The alloy exhibits exceptional creep strength compared to current commercial Fe-Ni-Cr and Ni-Cr-Fe alloys such as 253MA, RA330, 800H, 600 and 601. Major characteristics and attributes of the alloy including the alloy's mechanical properties and high temperature corrosion resistance are presented.

Fe-Ni-Cr ALLOYS, such as austenitic stainless steels^{1,2}, alloy 800H^{3,4}, and Ni-Cr-Fe alloys such as alloy 600 have been widely used for elevated temperature applications. These alloys are used in various industries including heat treating, chemical and petrochemical processing, refining and power generation. One limiting factor in high-temperature components made from some of these alloys is creep-rupture strength. The development of an alloy with higher creep-rupture strength would yield a long list of benefits, including longer component life, decreased distortion problems, higher load bearing capability, and an opportunity to decrease thermal mass (e.g., cross-sectional area).

The use of nitrogen to increase creep-rupture strengths of the alloy has been studied in 800H-type alloy⁵ and has been used commercially in 253MA[®] alloy⁶. In a study by Diglio et al⁵, alloy 800H was modified by making small additions of B, Zr and N. It was shown in this study that the creep resistance of 800H can be increased when nitrogen is added, such that the atomic ratio of Ti:C:N is about 4:2:1. The study goes on to show that the increased strengthening effect is strongly due to finely dispersed intragranular particles. In another study of nitrogen strengthened alloys, Yu et al.⁶ characterized precipitation in 253MA alloy during creep. The 253MA alloy

is a 21Cr-11Ni austenitic stainless steel in which the combination of carbon and nitrogen contribute to high creep strength.

The current paper discusses a new Fe-37Ni-25Cr alloy strengthened by nitrogen combined with niobium, a strong nitride former. The alloy exhibits creep-rupture strengths significantly higher than those of commercial Fe-Ni-Cr and Ni-Cr-Fe alloys.

ALLOY DESCRIPTION

HAYNES[®] HR-120[™] alloy was developed based on the Fe-Ni-Cr-Nb-N system. The alloy composition comprised principally of 37%Ni, 25%Cr, 0.7%Nb, 0.2%N, and balance Fe was optimized to yield maximum strengthening in creep. Minor elements such as Al, Si, W and Mo were also optimized in terms of creep-rupture strength and forgeability of the alloy. The nominal composition of the alloy is listed in Table 1. The alloy exhibits a stable austenitic structure. The typical microstructure of the alloy in the annealed condition is shown in Figure 1, showing primary nitrides and carbonitrides.

MECHANICAL PROPERTIES

CREEP RUPTURE - The outstanding creep-rupture strength of HR-120 alloy can best be demonstrated in comparing creep curves for several Fe-Ni-Cr alloys tested under identical conditions. These results are illustrated in Figure 2. At 1600°F (870°C) and 7 ksi (48 MPa) for example, the rupture life of HR-120 alloy was at least 40 times that of several other Fe-Ni-Cr alloys including 800HT[®] alloy. The creep curve of HR-120 alloy exhibits a very low creep rate during the first 2000 hours of the test.

Figure 3 presents stress rupture life data for HR-120 alloy at 1400°F (760°C), 1600°F (870°C) and 1800°F (980°C). Comparative plots of the stress to cause rupture in 1000 and 10,000 hours for selected alloys

HAYNES and HR-120 are registered trademarks of Haynes International, Inc.
253MA is a registered trademark of Avesta Jernverks Aktiebolag
RA330 is a registered trademark of Rolled Alloys Inc.
800HT is a registered trademark of Inco Alloys International, Inc.

Table 1 - Nominal Chemical Composition (weight percent) of HR-120™ alloy

Ni	Fe	Cr	Cb	N	Co	Mo	W	Si	Al	C	B
37	Bal	25	0.7	0.20	3*	2.5*	2.5*	0.6	0.1	0.05	0.004

* Maximum

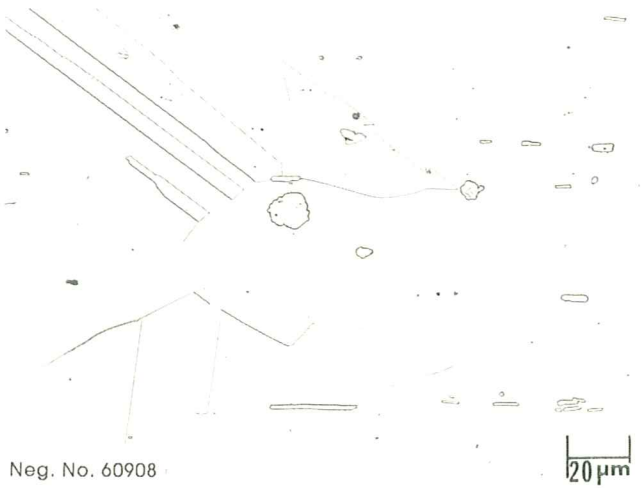


Fig 1 - Mill-Annealed microstructure of HR-120™ plate.

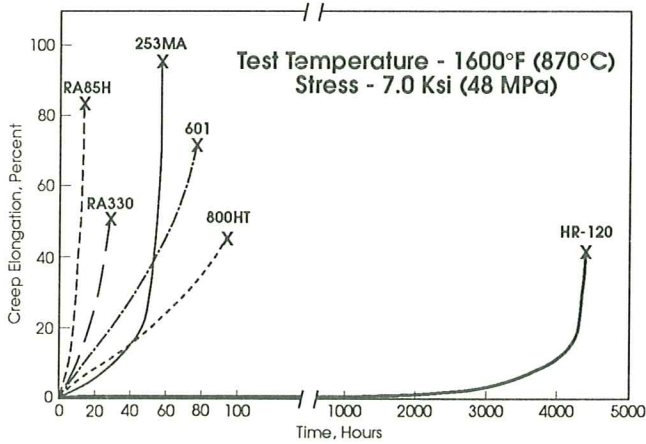


Fig. 2 - Creep curves for several alloys tested under identical conditions.

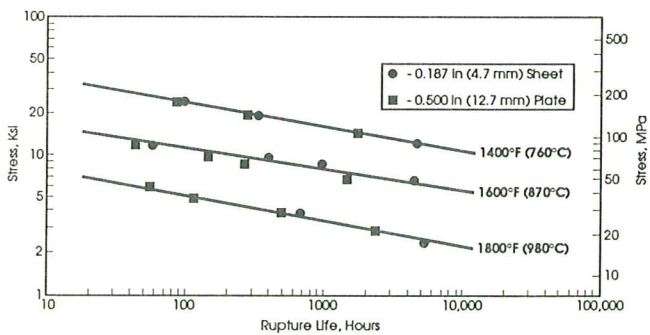
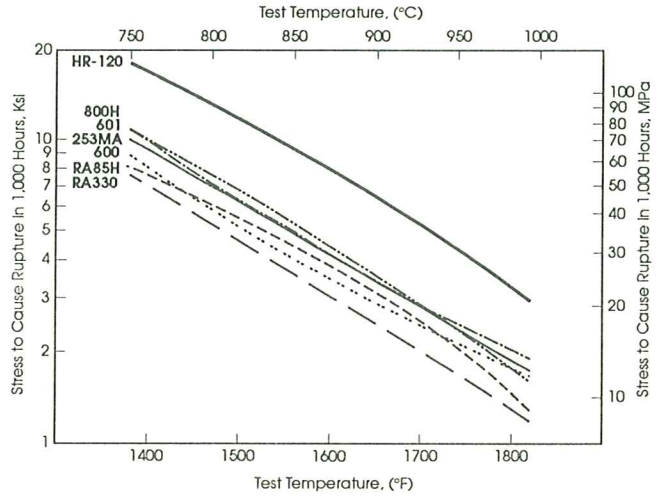
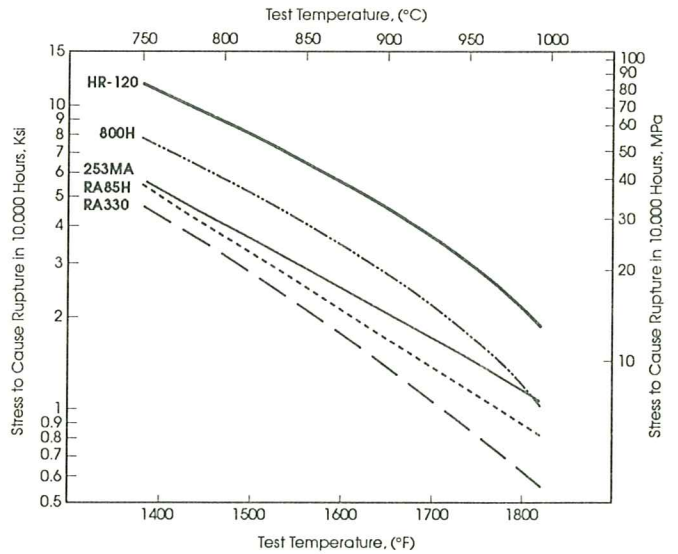


Fig. 3 - Stress rupture life of hot rolled and annealed HR-120 alloy.

are shown in Figure 4. The significant strength advantage of the nitrogen strengthened HR-120 alloy over current commercial alloys is clearly demonstrated. Included in Figure 4 is the nitrogen strengthened 253MA⁶ alloy which is substantially weaker than HR-120 alloy. The data for HR-120 alloy also indicates that it is stronger than the nitrogen modified 800H alloy discussed by Diglio et al.⁵



(a)



(b)

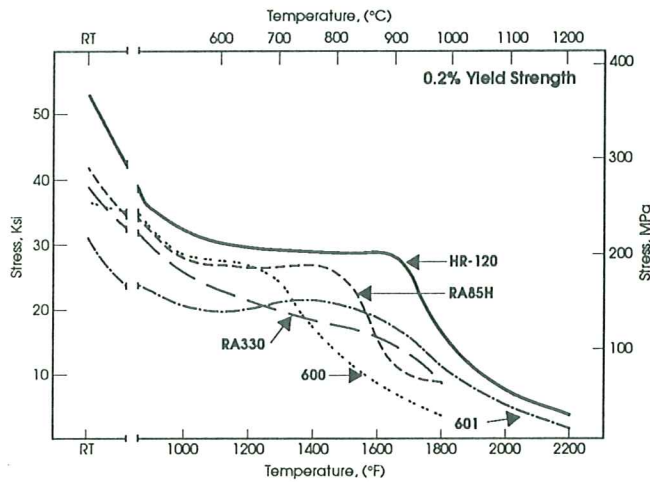
Fig. 4 - Stress to cause rupture in (a) 1000 hours, and (b) 10,000 hours.

The nitrogen modified alloy required about a 6.5 ksi (45 MPa) stress to cause rupture at 1470°F (800°C) compared to about 8.8 ksi (61 MPa) at the same temperature for HR-120 alloy.

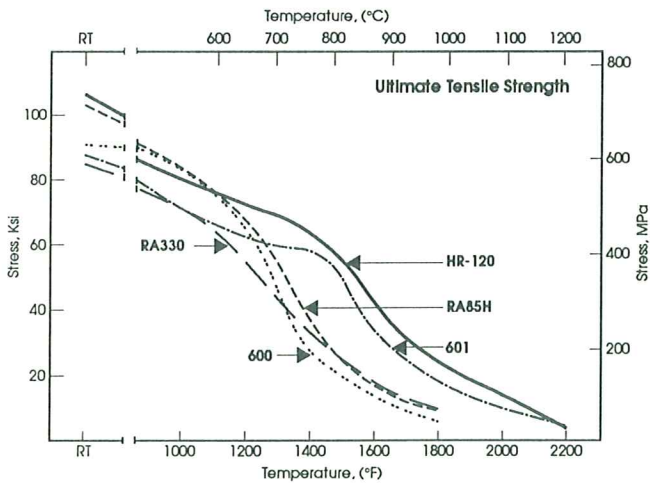
TENSILE PROPERTIES - The room temperature properties listed in Table 2 show that mill annealed HR-120 alloy exhibits good ductility and toughness with strength levels somewhat higher than those of typical austenitic stainless steels. The tensile strength of type 310 typically runs around 95 ksi (655 MPa) and the yield strength about 45 ksi (310 MPa). The elevated tensile properties are shown in comparative plots in Figure 5.

Table 2 - Typical Room Temperature Properties for Mill Annealed HR-120 Bar and Plate

Tensile Strength	106,900 psi (737 MPa)
0.2% Yield Strength	50,300 psi (347 MPa)
Elongation	51%
Hardness	88 R _B
Charpy V Notch	136 ft-lbs (184J)



(a)



(b)

Fig. 5 - Tensile properties of several commercial alloys; (a) 0.2% yield strength, (b) ultimate tensile strength.

THERMAL STABILITY - The thermal stability of the alloy was evaluated by performing tensile tests at room temperature following 1000 hour exposures at 1200°F (650°C), 1400°F (760°C) and 1600°F (870°C). The tensile test results are given in Table 3. The reduction in room temperature ductility is presumably attributed to precipitation of M₂₃C₆ carbides identified by x-ray diffraction. The x-ray diffraction results also indicated the presence of nitride-phases. Transmission electron microscopy studies are currently being performed to provide a more complete microstructural characterization. Typical microstructures after aging for 1000 hours at the three temperatures are shown in Figure 6. The precipitated phases can be eliminated by annealing the aged samples at 2250°F (1230°C), thereby restoring the alloy's good ductility.

ENVIRONMENTAL RESISTANCE

OXIDATION RESISTANCE - The oxidation resistance of the alloy was evaluated by performing static oxidation tests at 1800°F (980°C) and 2000°F (1090°C) in flowing air (25 mm/s). The samples were cycled to room temperature once a week for a total of six cycles over 1008 hours. After exposure, the samples were cathodically descaled and weighed to calculate the metal loss. Optical metallography is used to determine the depth of internal attack.

The results of the static oxidation tests are summarized in Table 4. At the test temperatures, the alloy is comparable to many other commercial Fe-Ni-Cr alloys such as 253MA and 800H, but not as good as the Ni-Cr-Fe alloys such as 600 and 601.

CARBURIZATION RESISTANCE - Carburization of high temperature alloys can result in embrittlement and eventual failure. Gas streams containing carbon monoxide and/or hydrocarbon gas are likely to carburize metals or alloys at elevated temperatures. The carburization resistance of the alloy was evaluated by performing pack carburization tests in graphite. The pack carburization tests were performed at 2000°F (1090°C) for 55 and 100 hours. The samples were evaluated in terms of carbon pick-up per unit area and microstructural changes.

The test results⁷, summarized in Table 5, indicate that HR-120 alloy has a carburization resistance better than alloys RA330 and 253MA. This is also clearly revealed by microstructural examination. Figure 7 shows little carburization for HR-120 alloy compared to alloys RA330 and 253MA, which were shown to be carburized through thickness. The HR-120 alloy however has a similar carburization resistance as RA85H[®] alloy.

SULFIDATION RESISTANCE - Sulfur is frequently present in many industrial environments. As a result, sulfidation attack often causes equipment failure^{8,9}. Recent work by Norton et al.¹⁰ evaluated the sulfidation resistance of HR-120 alloy. The tests were carried out in H₂-7%CO-1.5H₂O-0.6%H₂S at 1290°F (700°C). Gravimetric results of the test are summarized in Figure 8¹⁰. The results indicate the superior

RA85H is a registered trademark of Rolled Alloys Inc.

Table 3 - Room Temperature Tensile Properties Following 1000-Hour Isothermal Exposures

Condition	Ultimate Tensile Strength		0.2% Yield Strength		%El.
	Ksi	MPa	Ksi	MPa	
Annealed	106.5	734	45.6	314	50.0
Aged at 1200°F (650°C)/1000 hrs	107.1	38	48.1	332	33.4
Aged at 1400°F (760°C)/1000 hrs	102.6	707	49.0	338	14.4
Aged at 1600°F (870°C)/1000 hrs	92.7	639	49.1	338	10.6

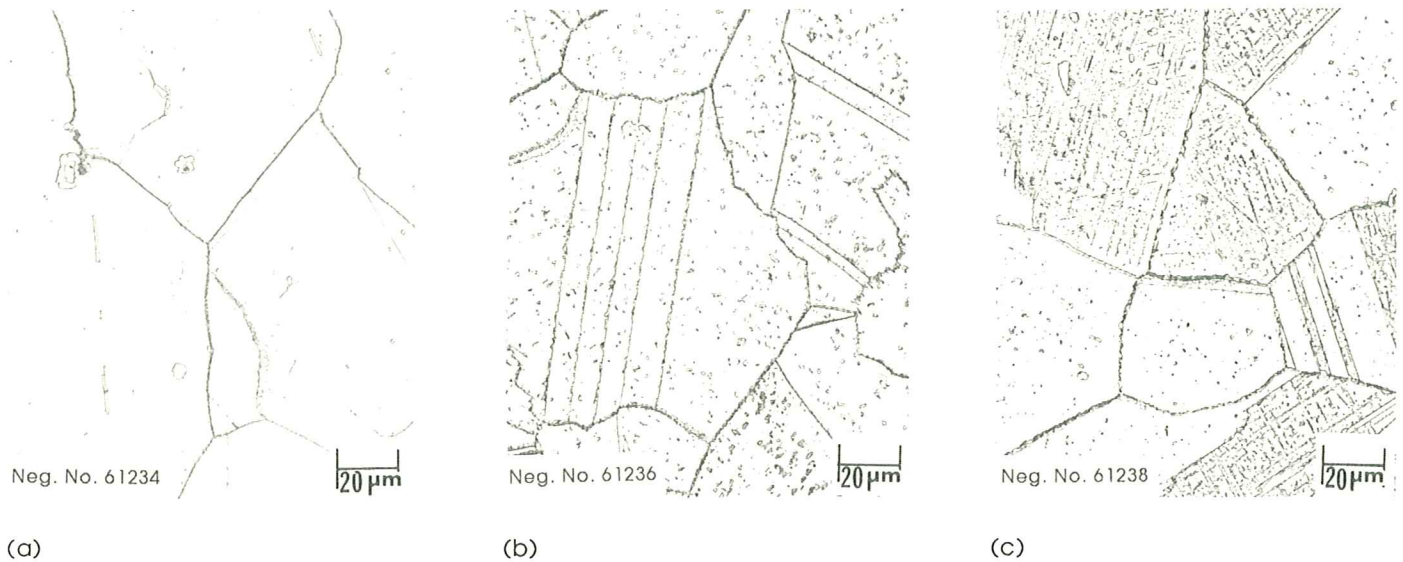


Fig. 6 - Typical optical photomicrographs of HR-120 plate following 1000 hours isothermal exposures at (a) 1200°F (650°C), (b) 1400°F (760°C) and (c) 1600°F (870°C).

Table 4 - Comparative Oxidation Resistance in Flowing Air - 1008-Hour Exposure at Temperature -

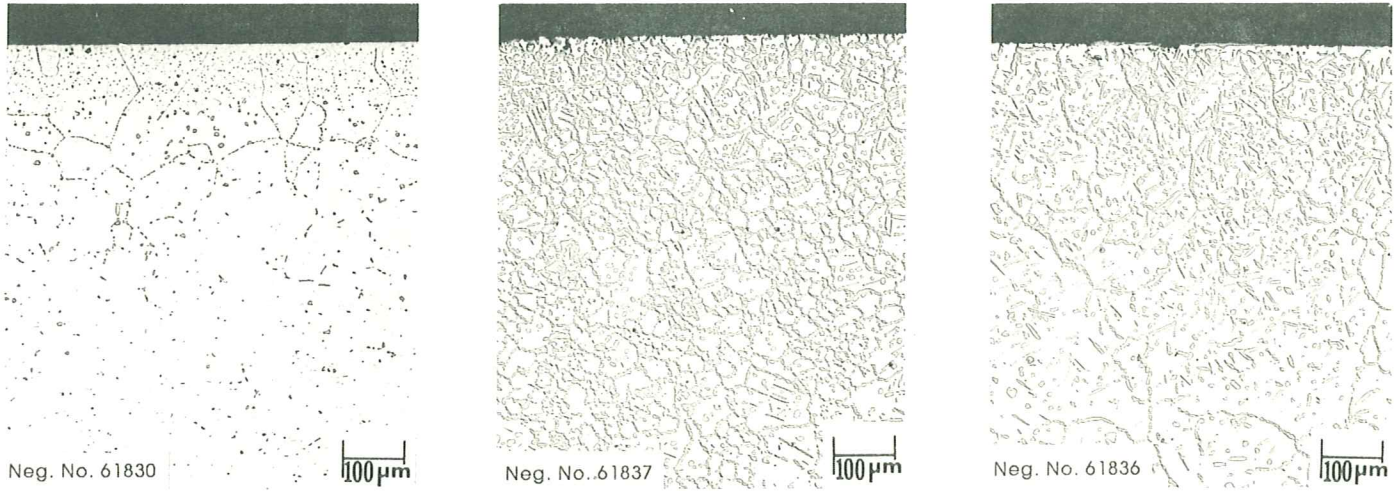
Material	1800°F (980°C)				2000°F (1090°C)			
	Avg. Metal Metal loss		Affected		Avg. Metal Metal Loss		Affected	
	mils	mm	mils	mm	mils	mm	mils	mm
Alloy 600	0.3	.008	.09	.023	1.1	.028	1.6	.041
601 alloy	0.5	.013	1.3	.033	1.2	.030	2.6	.066
RA330 alloy	0.4	.010	4.3	.109	0.8	.020	6.7	.17
Alloy 800H	0.9	.023	1.8	.046	5.4	.14	7.4	.19
HR-120 alloy	0.3	.008	3.7	.094	1.2	.030	7.7	.19
253MA alloy	1.3	.033	2.9	.074	0.7	.018	8.2	.21
RA85H alloy	0.5	.013	8.2	.21	2.9	.074	25.9	.66

Metal Affected = Metal Loss + Internal Attack

Table 5 - Results of Pack Carburization Tests at 2000°F (1090°C)(from Barnes')

Material	Carbon Absorption (mg/cm ₂)	
	55-Hour Test	100-Hour Test
HR-120 alloy	0.2	0.5
RA85H alloy	0.3	0.8
RA330 alloy	3.3	5.5
253MA alloy	4.1	12.8

* Tests conducted in graphite



a. HR-120 alloy

b. 253MA alloy

c. RA330 alloy

Note: carburized to center of specimen

Note: carburized to center of specimen

Fig. 7 - Typical carburized microstructures after 100 hours at 2000°F in graphite.

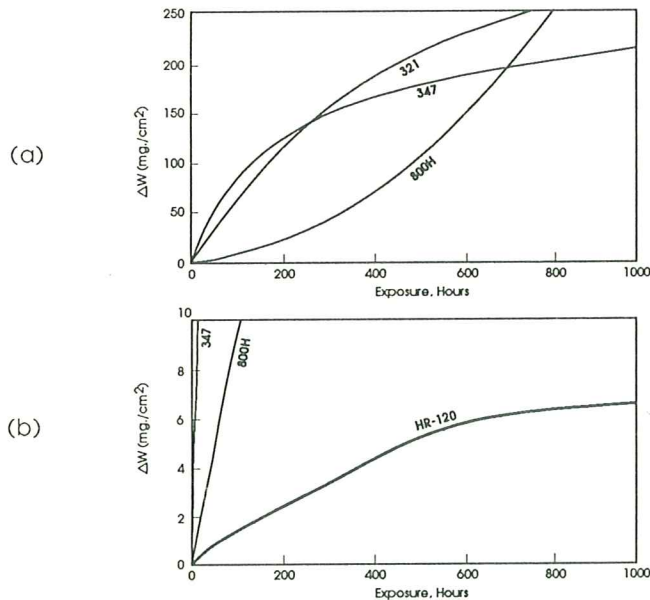


Fig. 8 - Gravimetric data for alloys tested at 1292°F (700°C) in H₂-7%CO-1.5H₂O-0.6H₂S. (from Norton et al.¹⁰)

(a) Type 321, Type 347 and alloy 800H

(b) Type 347, alloy 800H and HR-120 alloy

performance of HR-120 alloy as compared to Type 347 and alloy 800H. They¹⁰ observed that the stainless steel and alloy 800H had formed Fe-rich sulphides whereas Cr-rich sulfides were generally observed on the HR-120 alloy. Underneath the Cr-rich sulphides was a Cr₂O₃ scale.

HOT CORROSION - Hot corrosion is an accelerated oxidation or sulfidation attack due to a molten salt deposit. This form of corrosion is seen in gas turbines as well as in other industrial environments. The hot corrosion resistance of this alloy was evaluated by performing laboratory burner rig testing. The burner rig used No. 2 fuel oil with a sulfur content of about 1 wt% and air to generate the test environment. The air-to-fuel ratio was maintained at 35 to 1. The test was run at 1650°F (900°C) for 500 hours with a two-minute cooling cycle to less than 400°F (205°C) every hour. During testing a synthetic sea salt solution (ASTM D1141-52) was continuously injected into the combustion zone. Figure 9 shows the appearance of the specimens after testing. Specimens of alloys 253MA, RA85H, RA330, and 800H were essentially destroyed. On the other hand, the HR-120 alloy specimen still looks extremely good, showing little attack.

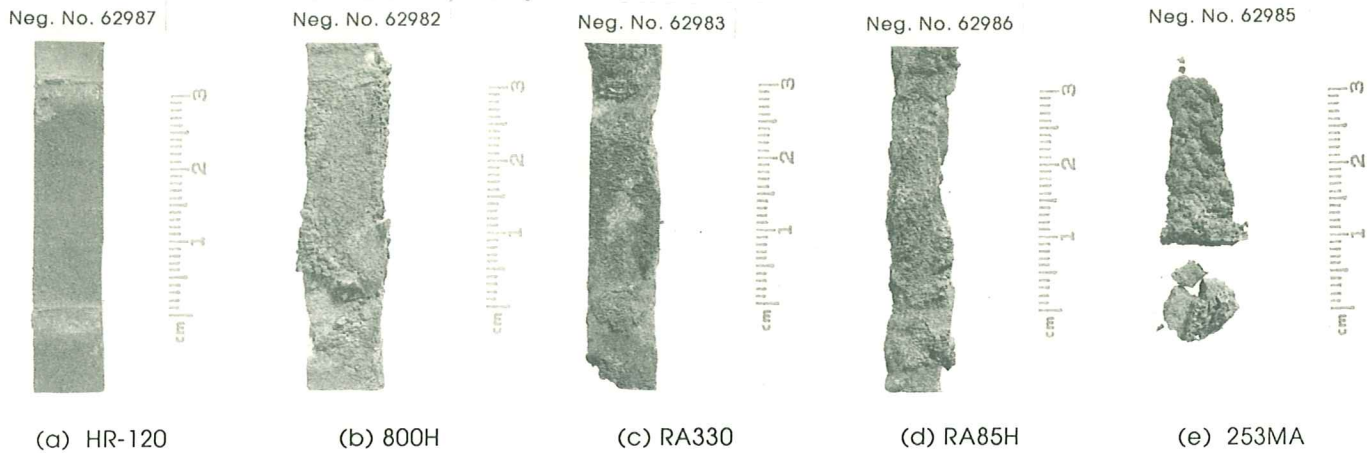


Fig. 9 - Hot corrosion test specimens after exposure at 1650°F (900°C) for 500 hours in 50 ppm seasalt and 1% sulfur fuel.

FABRICATION AND WELDING

HR-120 alloy has good formability, similar to that of austenitic stainless steels. The alloy is readily weldable using 556™ filler metal. The weldability and mechanical properties of 556 filler metal are described elsewhere¹¹. The weldability of HR-120 alloy using 556 filler metal was investigated by performing restrained plate weldability testing. Weldments were produced using gas tungsten arc (GTAW), gas metal arc (GMAW), and shielded metal arc (SMAW) welding processes. The 556 filler metal was used with the GTAW and GMAW processes. The SMAW process incorporated MULTIMET® coated electrodes which

are similar in properties to the 556 filler metal. The weldments consisted of 1/2-inch thick plates butt welded using a single-V groove. Figure 10 shows the GTAW weldment. Testing included guided bend testing and transverse (cross-weld) tensile testing.

The results of testing were, in all cases favorable. The bend test samples were bent with a radius twice the thickness and, for all the weldments, passed per ASME Section IX of the Boiler and Pressure Vessel Code. Tensile tests were run at both room temperature and 1800°F (980°C). In all cases the samples fractured in the parent metal indicative of 100% joint efficiency. The tensile test results for the GTAW weldment are presented in Table 6 and the fractured samples in Figure 11. Other testing has shown that HR-120 alloy can be autogenously welded (no filler metal added) up to at least 1/4-inch thick.

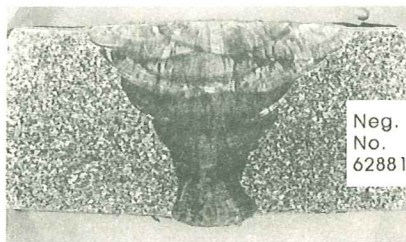


Fig. 10 - HR-120 plate, 0.5 inch (13mm) thick, gas tungsten arc welded (GTAW) using 556 filler metal.

Table 6 - Tensile Properties of Transverse Weld Specimens Consisting of HR-120 Plates Joined with 556 Filler Metal¹

Test Temperature		Ultimate Tensile Strength		0.2% Yield Strength		% EI ²
°F	°C	Ksi	MPa	Ksi	MPa	
RT	RT	110.8	764	60.0	418	44.8
1800	980	22.4	154	21.5	148	34.8

¹ Gas Tungsten Arc Welding (GTAW) process

² Calculated using adjusted gauge length - all specimens fractured in the HR-120 parent metal



Neg. No. 63476

(a)



Neg. No. 63477

(b)

Fig. 11 - Transverse weld tensile test specimens consisting of HR-120 plate and 556 filler metal.

(a) tested at room temperature

(b) tested at 1800°F (980°C)

6. M. Yu, R. Sandstrom, B. Lehtinen and Connie Westman, "Formation of Precipitates in the Austenitic Stainless Steel 253MA During Creep", Scandinavian J. of Metallurgy, 1987.
7. J. J. Barnes, Unpublished results, Haynes International, Inc., 1991.
8. Metals Handbook, Ninth Edition, Vol. 13, Corrosion, ASM International, Metals Park, OH 44073.
9. G. Y. Lai, J. of Metals, Vol. 37, No. 7, July 1985, p. 14.
10. J. F. Norton, F. G. Hodge and G. Y. Lai, "A Study of the Corrosion Behavior of Some Fe-Cr-Ni and Advanced Ni-Based Alloys Exposed to Sulfidising/Oxidizing/Carburising Atmosphere at 700°C", Kluwer Academic Publishers, Proceedings of a conference held in Liege, Belgium, 24-27 Sept. 1990.
11. S. C. Ernst and G. Y. Lai, "An Fe-Ni-Co-Cr Filler Metal Joining for Dissimilar High Temperature Alloys", ASM International, Metals Park, OH 44073, Proceedings of an International Conference, Phoenix, AZ, 17-19 April 1990.

SUMMARY

HR-120 alloy, a new nitrogen strengthened Fe-Ni-Cr-Cb alloy, was developed for elevated temperature applications. The alloy has been found to exhibit exceptionally good creep-rupture strengths, significantly higher than those of commercial Fe-Ni-Cr (e.g., alloy 800H) and Ni-Cr-Fe (e.g., alloy 600) alloys. The alloy also exhibits good environmental resistance, particularly in sulfidizing and carburizing atmospheres.

REFERENCES

1. L. Colombier and J. Hochmann, "Stainless and Heat Resisting Steels", Edward Arnold Publishers Ltd, London, 1967.
2. F. B. Pickering, "Physical Metallurgy of Stainless Steel Developments", Int. Metals Rev., December 1976.
3. M. A. Cordovi, "Existing and Potential Applications for Alloy 800", Alloy 800, North-Holland Publishing Co., 1978.
4. J. Orr, "A Review of the Structural Characteristics of Alloy 800", Alloy 800, North-Holland Publishing Co., 1970.
5. M. R. Diglio, H. Straube, K. Spiradek and H.-P. Degischer, "Improving the Creep Resistance of Alloy 800", Kluwer Academic Publishers, Proceedings of a conference held in Liege, Belgium, 24-27 Sept. 1990.

