



The Society shall not be responsible for statements or opinions advanced in papers or discussion at meetings of the Society or of its Divisions or Sections, or printed in its publications. Discussion is printed only if the paper is published in an ASME Journal. Authorization to photocopy material for internal or personal use under circumstance not falling within the fair use provisions of the Copyright Act is granted by ASME to libraries and other users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service provided that the base fee of \$0.30 per page is paid directly to the CCC, 27 Congress Street, Salem MA 01970. Requests for special permission or bulk reproduction should be addressed to the ASME Technical Publishing Department.

Copyright © 1996 by ASME

All Rights Reserved

Printed in U.S.A.

SEVERAL MODERN WROUGHT SUPERALLOYS FOR GAS TURBINE APPLICATIONS

George Y. Lai
Haynes International, Inc.
1020 West Park Avenue
Kokomo, IN 46904 USA



ABSTRACT

The present paper discusses several modern wrought superalloys that are being used for various hot gas path components in modern gas turbines. HAYNES® 230™ alloy (Ni-22Cr-14W-2Mo) is used for combustors and transition pieces to replace an old combustor alloy, HASTELLOY® X alloy (Ni-22Cr-19Fe-9Mo), because of higher creep-rupture strength, better oxidation resistance, higher low-cycle fatigue resistance, and other improved properties. The alumina forming HAYNES 214™ alloy (Ni-16Cr-3Fe-4.5Al-Y) replaces HASTELLOY X for honeycomb seals because of its superior oxidation resistance. HAYNES 242™ alloy (Ni-8Cr-25Mo), strengthened by a long-range ordered phase Ni₂(Cr,Mo) with low thermal expansion and high strength, is used for turbine casings and seal rings. A less expensive, nitride-strengthened Fe-Ni-Cr alloy, HAYNES HR-120™ alloy, offers an attractive upgrade to many stainless steels and some Ni-base alloys for less demanding, hot section components.

INTRODUCTION

Wrought superalloys play an important part in the construction of hot section components, such as, combustor and transition piece, for the gas turbine because of their high degree of fabricability. With the turbine entry temperatures for the gas stream reaching 1200°C or higher in modern gas turbines, these alloys are required to exhibit higher creep-rupture strengths, higher oxidation resistance, higher fatigue resistance, better thermal stability and better repairability. HASTELLOY X alloy, developed in the mid-1950s, has been the most widely used combustor alloy. In the late 1960s, a cobalt-base combustor alloy, HAYNES 188 alloy, was developed primarily to meet the increased operating temperature requirements for the gas turbines in military jets. In response to the cobalt crisis in the late 1970s, a nickel-base alloy, HAYNES 230 alloy, was developed in the early 1980s, with its creep-rupture strength approaching that of the Co-base alloy 188. Alloy 230 has since become a major alloy for combustor liners and transition pieces in modern gas turbines.

Almost all the high temperature wrought alloys used in gas turbines form chromium oxide scales for protection against oxidation. In the early 1980s, a nickel-base alloy, HAYNES 214 alloy, that forms aluminum oxide scales was developed. One major application for this alloy in modern gas turbines is a honeycomb seal to replace the widely used HASTELLOY X honeycomb seals, particularly for those operating at higher temperatures.

HAYNES and HASTELLOY are registered trademarks of Haynes International, Inc.; 230, 214, 242 and HR-120 are trademarks of Haynes International, Inc.

Another important components are casings and rings for turbines where alloys with low thermal expansion characteristics and high strength are of primary importance. A new high strength, low thermal expansion alloy, HAYNES 242 alloy, was developed in the late 1980s. The alloy is currently being used in modern gas turbines.

Many hot gas path components, which are subject to less severe operating conditions and are currently made of stainless steels and Fe-Ni-Cr alloys, can be upgraded with an advanced Fe-Ni-Cr alloy, HAYNES HR-120 alloy, without paying the prices of Ni- and Co-base superalloys. HR-120 alloy, developed in the early 1990s, exhibits tensile and creep-rupture strengths significantly higher than stainless steels (e.g., Type 310 SS) and some Ni-base alloys, such as, HASTELLOY X, RA 333[®], etc.

The above four modern wrought superalloys and their major characteristics and properties are discussed in the following sections. Nominal chemical compositions of these alloys are tabulated in Table 1.

HAYNES 230 ALLOY

The alloy was developed to achieve the best combination of tensile and creep-rupture strength, low cycle fatigue resistance, thermal stability, oxidation resistance and resistance to grain coarsening.⁽¹⁻³⁾ High tensile and creep-rupture strengths are achieved by the use of a significant level of tungsten for a solid solution strengthening element. Tungsten is known to diffuse much more slowly than Mo in nickel⁽⁴⁾ and also to lower the stacking fault energy of nickel.⁽⁵⁾ Both these factors would contribute to high temperature strength. In addition, control of the atomic ratio of chromium to the sum of molybdenum and one-half tungsten promotes the formation of $M_{23}C_6$ during elevated temperature exposure, further enhancing the alloy's creep-rupture strength.⁽¹⁾ Figure 1 illustrates the 1% creep strength of 230 alloy in comparison with alloys 188 and X, showing that 230 alloy is approaching the cobalt-base alloy 188 and is significantly stronger than alloy X, a Ni-Cr-Fe-Mo alloy.

The fatigue strength of the alloy is optimized by the control of the grain size to a range of ASTM 4-6. The fatigue behavior of this alloy has been extensively studied.⁽⁶⁻⁸⁾ Alloy 230 exhibits higher low cycle fatigue strength than alloys X and 617 at 650, 760 and 980°C.⁽⁷⁾ For example, at 980°C and 0.25 % total strain range, the number of cycles to failure was 112,957 for 230 alloy as opposed to 29,346 and 5,924 for alloys X and 617, respectively. The alloy also exhibits good thermal stability with about 34% or more of room temperature tensile elongation after aging at 650, 760 and 870°C for 16,000 hours.⁽⁹⁾ Aging at intermediate temperatures of 650, 760 and 870°C resulted in the precipitation of $M_{23}C_6$ carbides. No precipitation of intermetallic compounds such as mu or sigma phases were observed after 16,000 hours of aging at these temperatures. The chemistry of each heat is adjusted using an electron vacancy, N_v , control method to avoid the formation of these intermetallic compounds. Finally, the significant level of tungsten promotes the formation of primary, tungsten-rich M_6C carbides which resist

RA333 is a registered trademark of Rolled Alloys

solutioning during solution heat treatment, thus helping to control grain size and resist grain coarsening. As a result, the alloy is normally annealed at 1230°C, which is about 50-100°C higher than many wrought superalloys. Resisting grain coarsening is an important characteristic in that in case of temperature overshoot or hot spots the alloy is less prone to grain coarsening, which is not a desirable microstructural change during service.

The optimization of chromium and control of minor alloying elements of manganese and silicon with the addition of lanthanum resulted in an alloy with excellent oxidation resistance.⁽¹¹⁾ The alloy was recently found to be very resistant to nitridation in combustion environments.⁽¹⁰⁾ The observation recently made by Swaminathan and Lukezich indicated severe nitridation attack at the "hot spot" of the transition piece of a land-based gas turbine.⁽¹¹⁾ Recent studies by Lai using a high velocity dynamic burner rig to simulate the environmental conditions of the combustion liner and transition piece have shown significant nitridation attack under these conditions.⁽¹⁰⁾ These tests were conducted in a high velocity gas stream (0.3 Mach or 100 meter/sec) at 980°C for 1000 hours with severe thermal cycling by rapidly cooling the test specimens to less than 260°C for two minutes once every 30 minutes. The major findings from these tests were briefly summarized below. Alloys, such as alloys 617 and 263, containing 1 to 2% of Al or Ti are very susceptible to nitridation attack by forming aluminum nitrides or titanium nitrides. In these tests, the bulk nitrogen content was found to increase from the initial value of 0.03% (wt) to 0.52% for alloy 617 and from 0.004% to 0.42% for alloy 263. Alloys containing little or no Al or Ti are also susceptible to nitridation attack by formation of chromium nitrides. With more iron in the alloy, nitridation attack was more aggressive for alloy X, which formed significant amounts of chromium nitrides as a result of testing, with the bulk nitrogen content increasing from 0.04% to 0.57%. Wrought alloys containing 0.4-0.6% nitrogen would be brittle and difficult to weld repair as well. Alloy 230 was not significantly affected, with very little nitrogen pick up (from 0.05 to 0.06%). The alloy forms only small amounts of chromium nitrides. The microstructures of alloys 230 and 617 after testing are illustrated in Fig. 2. Alloy 230 forms fine $M_{23}C_6$ carbides during testing at 980°C, and exhibits a zone depleted in carbides underneath oxide scales, typical of long-term aged micro-structure. Chromium nitrides are large, blocky phases, marked by arrows. Alloy 617 shows long needle aluminum nitrides as well as some blocky chromium nitrides underneath oxide scales.

HAYNES 214 ALLOY

The major characteristic of this alloy is that it forms a very adherent aluminum oxide scale when heated to elevated temperatures. When the high temperature component is constructed out of thin foils, oxidation becomes a critical issue. One important component is a turbine seal ring assembly, which controls the turbine tip clearance for improving the thermal efficiency. The seal ring assembly is typically constructed out of a honeycomb seal brazed onto a superalloy casing. The honeycomb seal is generally constructed out of HASTELLOY X foils. Alloy 214 honeycomb seals are now being used to replace alloy X honeycomb seals operating at higher temperatures because of the superior oxidation resistance of the alumina-forming, alloy 214. The oxidation behavior of 214 alloy can be found elsewhere.⁽¹²⁾ However, the superior oxidation resistance of 214 alloy honeycomb over that of alloy X honeycomb can be illustrated by a dynamic burner rig test, which was conducted at 954°C for 317 hours in a high velocity gas

stream (0.3 Mach or 100 meter/sec) with a 30 min thermal cycling. The alloy X honeycomb sample constructed out of 3 mil foils was completely destroyed after 154 hours of testing, while the alloy 214 honeycomb sample made of the foil of same thickness was basically unaffected by the test (317 hours). The samples after testing are shown in Fig. 3.

HAYNES 242 ALLOY

This alloy is based on a long-range ordered phase, $Ni_2(Cr, Mo)$, for strengthening, and the Ni-Mo system for low thermal expansion characteristics, with the control of chromium for oxidation resistance. The long range ordered phase, $Ni_2(Cr, Mo)$, developed by aging at $650^{\circ}C$, is shown in Fig. 4. Fig. 5 illustrates the creep-rupture strength of this alloy in comparison with several seal ring and casing alloys including alloy 909. Alloy 242 exhibits higher rupture strength than alloy 909. The thermal expansion coefficients of the alloy, however, are slightly higher than those of alloy 909, but are significantly lower than alloys X, S, 718. The properties of this alloy was described in an earlier paper.⁽¹³⁾ Furthermore, unlike Fe-Ni-Co type low thermal expansion alloys, alloy 242 is very resistant to cyclic oxidation up to $816^{\circ}C$ and is not susceptible to SAGBO (Stress Assisted Grain Boundary Oxidation), as shown in Fig. 6. Figure 6 illustrates the surface conditions of both 909 and 242 specimens after dynamic oxidation testing at $760^{\circ}C$, showing cracking of alloy 909 and no evidence of cracks developed on the 242 specimen. The 242 alloy is currently being used as turbine casings and rings.

HAYNES HR-120 ALLOY

One of the inventions of this advanced Fe-Ni-Cr alloy, HR-120 alloy, is the use of niobium (columbium) and nitrogen in combination with carbon to produce an alloy with both nitride- and carbide-strengthening. This alloy exhibits the creep-rupture strength significantly higher than typical Fe-Ni-Cr alloys, such as, Type 310 SS, 800H, RA 330, etc., and also some Ni-base alloys, such as alloy X, RA 333, alloy 601, etc. The comparison 10,000-h rupture strength for various alloys is shown in Table 2. A detailed discussion of the properties for this alloy can be found elsewhere.⁽¹⁴⁾ Since commercial introduction in 1990, the alloy has been successfully used as an upgrade to stainless steels, Fe-Ni-Cr alloys, such as alloy 800H, and some Ni-base alloys for various industries. Successful industrial application of HR-120 alloy, so far, includes heat treat retorts, muffles, baskets, and other components in heat treat industry, as high temperature calciners and rotary kilns for production of catalysts and mineral processing with operating temperatures up to $1090^{\circ}C$, and various components in boilers, incinerators and other industrial plants. The alloy offers an attractive upgrade to stainless steels and some Ni-base alloys, such as RA 333 and alloy X, for hot gas path components with less demanding service conditions.

SUMMARY

Four new wrought superalloys, 230, 214, 242 and HR-120 alloys, were reviewed in terms of their major characteristics and properties. Major applications for these alloys in modern gas turbines were also discussed. HAYNES 230 alloy with the best combination of tensile and creep-rupture strengths, fatigue resistance, thermal stability, oxidation resistance and resistance to grain

coarsening has become a major alloy for combustion liners and transition piece since its commercial introduction in the early 1980s. HAYNES 214 alloy with its superior oxidation resistance due to the formation of aluminum oxide scales is being used for honeycomb seals to replace HASTELLOY X honeycomb seals for operation at higher temperatures. HAYNES 242 alloy, a low thermal expansion alloy with high strength utilizing a long-range order strengthening phase, $Ni_2(Cr,Mo)$, and resistance to SAGBO, is being used for turbine casings and rings. A new high strength Fe-Ni-Cr alloy strengthened by carbides and nitrides, HR-120 alloy, with creep-rupture strength higher than even some of the Ni-base alloys such as alloys X and RA 333 is an attractive upgrade alloy for many hot gas path components with less demanding service conditions than those of the combustor and transition piece.

REFERENCES

1. D. L. Klarstrom, U. S. Patent 4,476,091
2. D. L. Klarstrom, H. M. Tawancy, D. E. Fluck, and M. F. Rothman, "A New Gas Turbine Combustor Alloy", International Gas Turbine Conference, ASME Paper 84-GT-70, New York, NY, ASME, 1984
3. D. L. Klarstrom, H. M. Tawancy, and M. F. Rothman, in Superalloys 1984, M. Gell, et al. eds., TMS-AIME, Seven Springs, PA, p. 553
4. A. Davin, V. Leroy, D. Coutsouradis, and L. Habraken, Cobalt, 19-6, 1963, p. 51
5. T. C. Tearnay, Jr. and N. J. Grant, Met. Trans. A, 13A, 10, 1982, p. 1827
6. D. L. Klarstrom and G. Y. Lai, in Superalloys 1988, S. Reichman, et al., eds., TMS-AIME, Seven Springs, PA, p. 585
7. S. K. Srivastava and D. L. Klarstrom, "The LCF Behavior of Several Solid Solution Strengthened Alloys Used in Gas Turbine Engines", International Gas Turbine Conference, ASME Paper 90-GT-80, Brussels, Belgium, ASME, 1990
8. K. S. Vecchio, M. D. Fitzpatrick, and D. L. Klarstrom, Met Trans. A, 26A, 1995, p. 673
9. D. L. Klarstrom, "The Thermal Stability of A Ni-Cr-W-Mo Alloy," Paper No. 407, Corrosion/94, NACE International, Houston, TX
10. G. Y. Lai, in Advanced Materials and Coatings for Combustion Turbines, V. P. Swaminathan and N. S. Cheruvu, eds., ASM International, Materials Park, OH, 1994, p. 113
11. V. P. Swaminathan and S. J. Lukezich, in Advanced Materials and Coatings for Combustion Turbines, V. P. Swaminathan and N. S. Cheruvu, eds., ASM International, Materials Park, OH, 1994, p. 99
12. G. Y. Lai, High Temperature Corrosion of Engineering Alloys, ASM International, Materials Park, OH, 1990
13. S. K. Srivastava and G. Y. Lai, "A New Low-Thermal-Expansion, High-Strength Alloy for Gas Turbines," International Gas Turbine Conference, ASME Paper 89-GT-329, Toronto, Canada, ASME, 1989
14. S. K. Srivastava, G. Y. Lai and T. L. Warner, in Heat-Resistant Materials II, K. Nateson, P. Ganesan and G. Lai, eds., ASM International, Materials Park, OH, 1995, p. 495.

Table 1 Nominal Compositions of the Four Wrought Superalloys Discussed in the Paper

Alloy	Nominal Composition (wt.%)							
	Ni	Cr	Fe	W	Mo	Al	C	Others
230™ alloy	Bal.	22	3*	14	2	0.3	0.10	0.02La, 0.015*B
214™ alloy	Bal.	16	3	-	-	4.5	0.05	0.01Y
242™ alloy	Bal.	8	2*	-	25	0.5*	0.03*	0.006*B
HR-120™ alloy	37	25	Bal.	2.5*	2.5*	0.1	0.05	0.7Cb, 0.2N

* maximum

Table 2 The 10,000-h rupture strengths for alloys HR-120, X, RA333, 310SS

Temp. °C	Stress (MPa) to Cause Rupture in 10,000h			
	HR-120	X	RA333	310SS
649	169	166	114	64
760	76	69	63	27
871	39	27	21	11
980	12.4	9.7	7.2	4.8

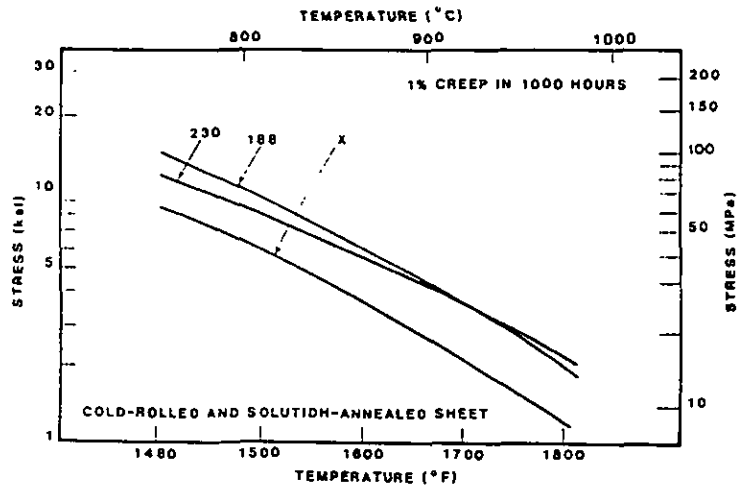


Fig. 1: The 1000-h 1% creep strength for alloys 230, 188 and X.

Downloaded from http://asmelibrarycollection.asme.org/ on 03/22/16 by guest on 03/22/16

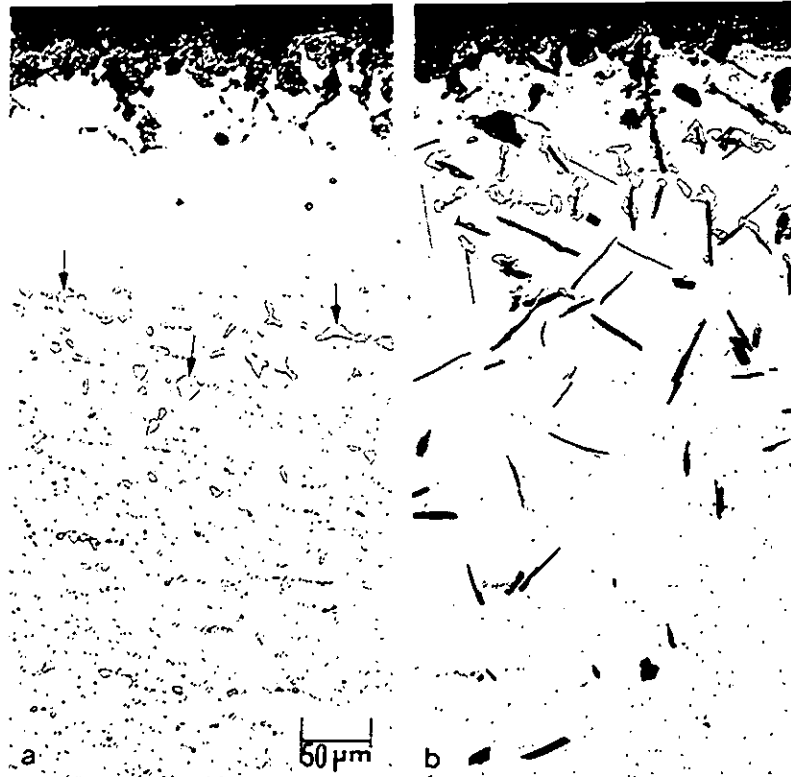


Fig. 2: Microstructures of 230 alloy (a) and alloy 617 (b) after burner rig testing at 980°C for 1000 hours with 30-min. thermal cycling.

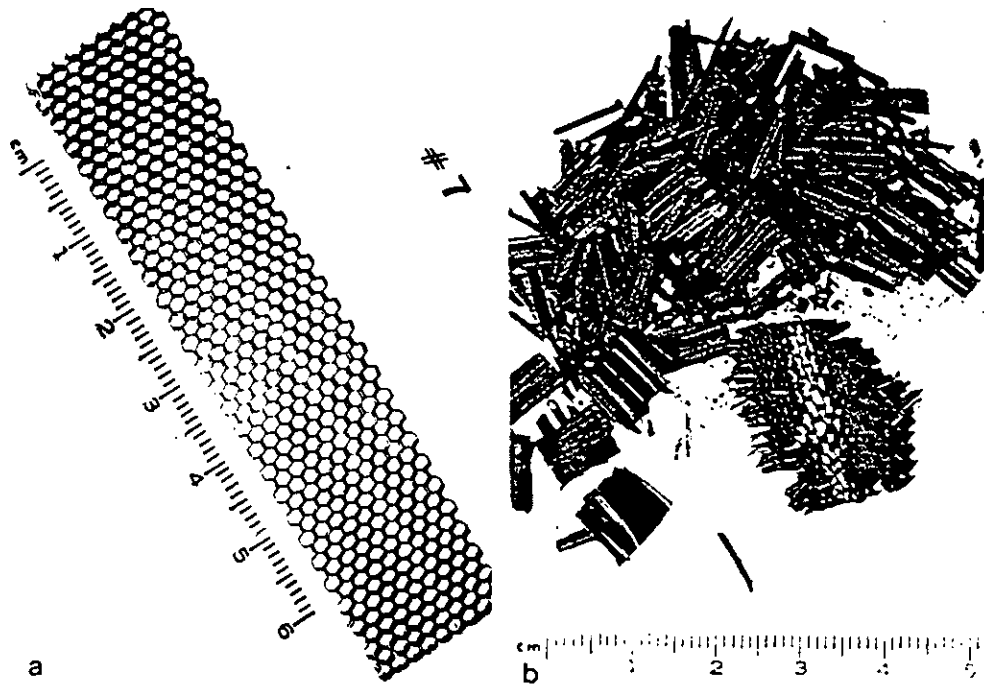


Fig. 3: Honeycomb samples of 214 alloy (a) and alloy X (b) after dynamic burner rig testing at 954°C for 317 hours for 214 alloy and for 154 hours for alloy X.

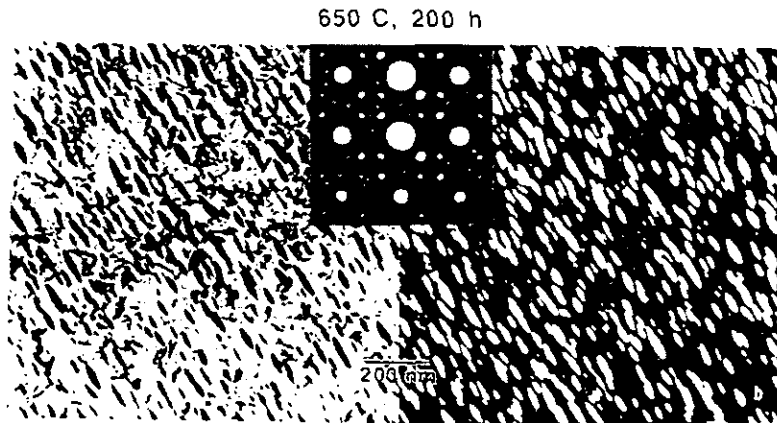


Fig. 4: TEM micrographs of 242 alloy aged at 650°C for 200 hours. Bright field image (left) and dark field image (right) of a long-range ordered phase $Ni_2(Cr,Mo)$, with a selected area diffraction pattern (insert).

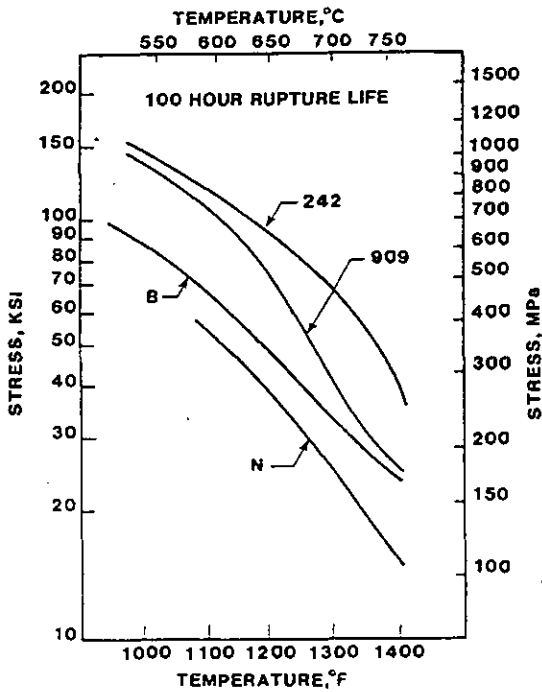


Fig. 5: The 100-h rupture strengths for alloys 242, 909, N and B.

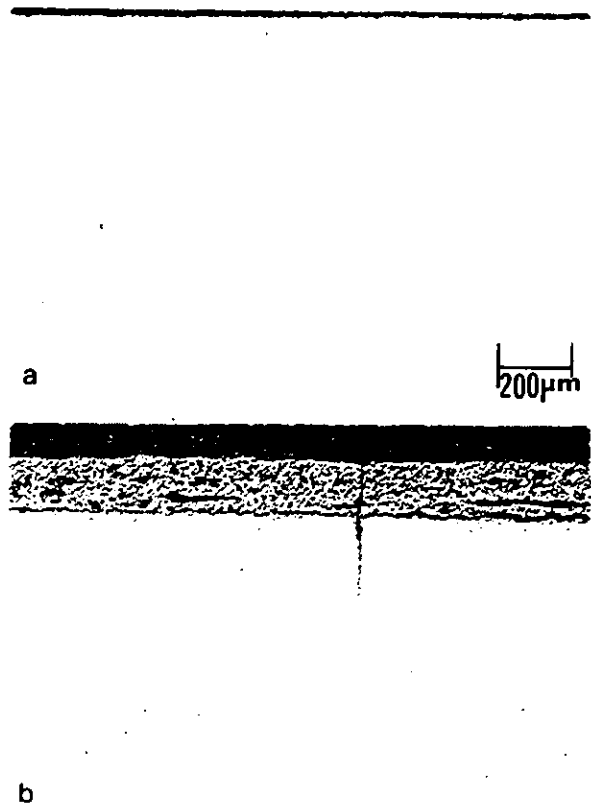


Fig. 6: Cross-sections of 242 alloy (a) and alloy 909 (b) after dynamic burner rig testing at 760°C for 500 hours with 30-min. thermal cycling.