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Nickel-Base Alloy Solutions for Ultrasupercritical Steam Power Plants

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Abstract

Significant research efforts are being performed in Europe, Japan and the U.S. to develop the technology to increase the steam temperature in fossil power plants in order to achieve greater efficiency and reduce the amount of greenhouse gases emitted. The realization of these advanced steam power plants will require the use of nickel-based superalloys having the required combination of high temperature creep strength, oxidation resistance, thermal fatigue resistance, thermal stability and fabricability. HAYNES[®] 230[®] and 282[®] alloys are two alloys that meet all of these criteria. The metallurgical characteristics of each alloy are described in detail, and the relevant high temperature properties are presented and discussed in terms of potential use in advanced steam power plants.

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1. Introduction

A number of efforts have been established in Europe, Japan and the United States to develop more efficient fossil fuel power plants by increasing steam temperatures and pressures [1]. These so-called ultrasupercritical steam power plants will operate with steam temperatures in the 700-760°C (1300-1400°F) temperature range with pressures above 24 MPa (3.5 ksi). Such conditions are well beyond the capabilities of current carbon and stainless steels, and, hence, the use of nickel-base alloys will be required in order to satisfy the long term service goals.

In the initial survey of materials, HAYNES[®] 230[®] alloy was identified as a candidate for a variety of components due to its high ASME Code allowable stresses in the temperature range of interest. Because the alloy is solid-solution strengthened, its use is facilitated since no special aging heat treatment is required after fabrication to engender strength. The alloy is noted for its excellent high temperature creep strength and

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oxidation resistance, and it is probably the most thermally stable solid-solution strengthened alloy currently available [2].

INCONEL[®] alloy 740, an age-hardenable nickel-base alloy, was also identified as a candidate material because of its potentially higher allowable stresses. However, the alloy is not thermally stable in the temperature range of interest, which may limit its use [2]. Recently, a new age-hardenable superalloy, HAYNES 282[®] alloy, was commercially introduced which offers the potential of even higher allowable stress levels than alloy 740 in addition to superior thermal stability [3,4]. The new alloy has creep strength competitive with R-41 alloy, but it offers much better formability and weldability.

2. Physical metallurgy

The compositions of 230 and 282 alloys are shown in Table 1 along. Among the nickel-based solid-solution strengthened alloys, 230 alloy is unique because it relies primarily on tungsten as the major strengthening element. Tungsten was selected because it diffuses more slowly in nickel than molybdenum, and, therefore, it enhances high temperature creep strength [2]. This solid-solution strengthened alloy also relies on the formation of chromium-rich $M_{23}C_6$ carbides which precipitate on and immobilize dislocations formed during high temperature creep. A small addition of boron is used to improve the lattice mis-match between the carbide and the face-centered cubic matrix, which improves the carbide stability. The alloy also forms large, tungsten-rich M_6C carbides during ingot solidification that get distributed throughout the microstructure during hotworking operations. Due to their high tungsten content, these carbides do not dissolve easily, and they serve as important second-phase obstacles for controlling the grain size of the alloy. The alloy is typically annealed in the temperature range of 1177 to 1232°C (2150 to 2250°F) to develop a grain size of ASTM 4-5. This grain size provides the best combination of creep and fatigue strength.

Table 1. Nominal compositions of 230, 282 and comparative alloys, wt.% (* max.)

Alloy	Ni	Co	Fe	Cr	Mo	W	Mn	Si	Al	Ti	C	B	Others
Solid-Solution Strengthened													
230	57	5*	3*	22	2	14	0.5	0.4	0.5*	0.1*	0.10	0.015*	La-0.02
X	47	1.5	18	22	9	0.6	1*	1*	0.5*	0.15*	0.10	0.008*	-
617	54	12.5	1	22	9	-	-	-	1.2	0.3	0.07	-	-
Age-Hardened													
282	57	10	1.5*	20	8.5	-	0.3*	0.15*	1.5	2.1	0.06	0.005	-
263	52	20	0.7*	20	6	-	0.4	0.2	0.6*	2.4*	0.06	0.005*	Al+Ti=2.6
740	48	20	0.7	25	0.5	-	0.3	0.5	0.9	1.8	0.03	-	Nb-2
WASPALLOY	58	13.5	2*	19	4.3	-	0.1*	0.15*	1.5	3	0.08	0.06	Zr-0.05

The age-hardenable alloys all depend on the formation of gamma-prime, $Ni_3(Al, Ti)$, for their strength. The (Al + Ti) content for 282 alloy is higher than for 263 alloy, which ensures that its high temperature creep strength will be better. Furthermore, its addition of 8.5% Mo in combination with the (Al + Ti) of 3.6% provides creep properties which exceed those of Waspaloy and which are competitive with R-41 alloy. The alloy is typically annealed in the temperature range of 1107 to 1149°C (2025 to 2100°F) to obtain a grain size of ASTM 4 – 4 ½ for optimum resistance to creep and low cycle fatigue. It is then given a two-step heat treatment consisting of 1010°C (1850°F)/2 hrs./AC + 788°C (1450°F)/8 hrs./AC. The first step is carried out at a temperature above the gamma-prime solvus temperature of 997°C (1827°F) primarily to form $M_{23}C_6$ carbides at the grain boundaries in the preferred morphology to resist grain boundary sliding during creep. The second step results in the formation of the matrix strengthening gamma-prime precipitates. Because the alloy contains titanium, a small quantity of titanium-rich MC carbides and carbonitrides can be found scattered throughout the microstructure.

3. Mechanical properties

3.1. Creep strength

The low strain creep strength of 230 alloy is quite good among the solid-solution strengthened alloys. This is illustrated in Figure 1 for a creep strain of 1% for plate. The alloy shows an advantage over the entire range shown, which makes it an attractive candidate for use in ultrasupercritical steam plants.

Among the age-hardened alloys, 740 alloy has been carefully examined because its creep strength is much higher than the solid-solution strengthened alloys. However, the introduction of HAYNES 282 alloy has provided an alloy with even better high temperature strength. This is shown in Figure 2, which compares the 1000 hour rupture strengths in a Larson-Miller format over the temperature range of 650-816°C (1200-1500°F). From the figure, it can be seen that 282 alloy provides a significant advantage over most of the range, and especially in the 700-760°C (1300°-1400°F) range of interest.

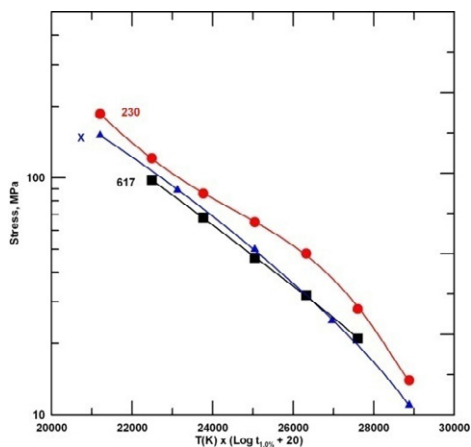


Fig.1. Comparison of 1% creep strengths of 230, X and 617 alloys (plate).

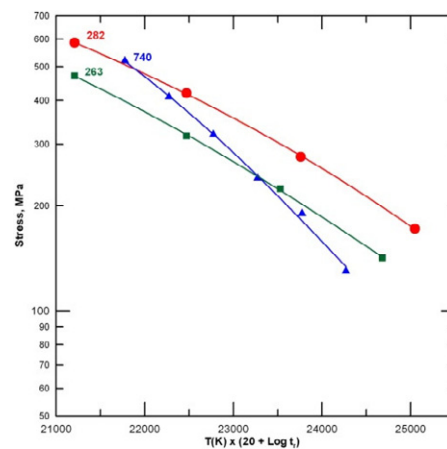


Fig. 2. Comparison of the 1000-hour stress rupture strengths of plate and bar.

Of particular note, is that the advantage of 740 alloy over 263 alloy declines rather rapidly within this temperature range, and at 760°C, 740 alloy is actually weaker than 263 alloy. This is probably due to the fact that 740 alloy contains no molybdenum to strengthen the matrix.

3.2. Fatigue properties

Among the solid-solution strengthened alloys, 230 alloy possesses outstanding fatigue strength. This is illustrated in Figure 3 for fully reversed, strain-controlled, low cycle fatigue at 760°C(1400°F) and 870°C(1600°F) at a frequency of 0.33 Hz [5] for plate. The alloy has also been shown to possess excellent resistance to thermal fatigue [6]. It was found to be superior to 617 alloy as shown in Figure 4 for plate samples. The advantage of 230 was also found to hold for welded samples. Resistance to thermal fatigue would be an important consideration for plant shutdown operations.

HAYNES 282 alloy has also been found to possess excellent resistance to low-cycle fatigue [7]. A comparison of 282 and 263 alloys is shown in Figure 5 for strain-controlled LCF at 815°C and a frequency of 0.33Hz. The thermal fatigue behavior of 282 has not yet been investigated.

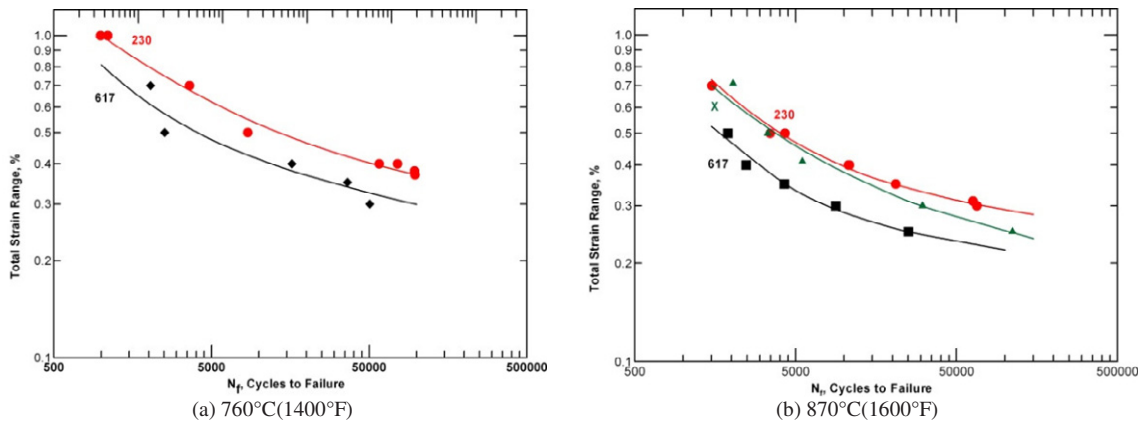


Fig. 3. Strain controlled (R=-1) lowcycle fatigue curves for 230, 617 and X alloys.

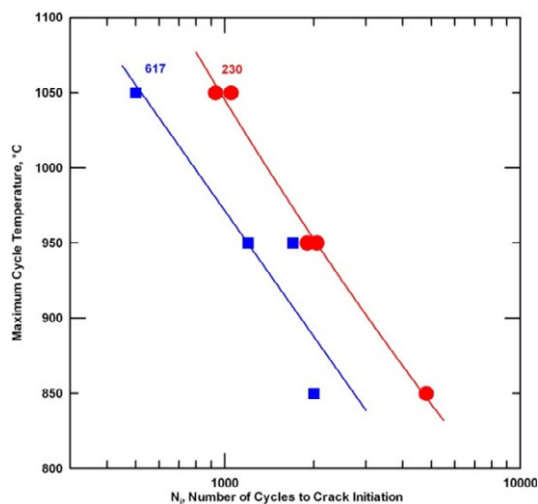


Fig. 4. Thermal fatigue crack initiation as a function of T_{max} for 230 and 617 alloys [5].

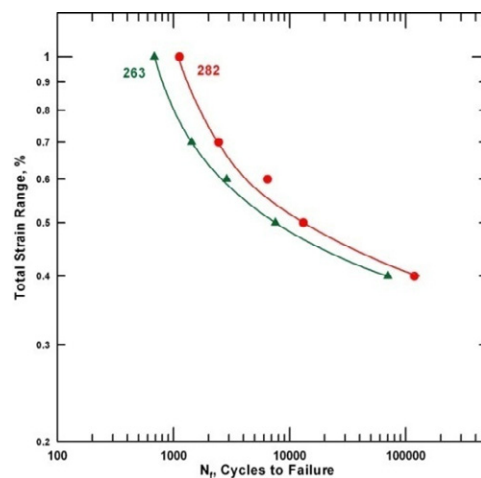


Fig. 5. Comparison of the LCF lives of 282 and 263 alloys at 815°C (1500°F) (sheet).

4. Oxidation resistance

HAYNES 230 alloy was formulated to have excellent resistance to oxidation with additions of 22% chromium in a nickel base along with minor additions of manganese, silicon and lanthanum [2]. During oxidation, the alloy develops a manganese-chromium spinel oxide which is very protective. Recent studies relevant to its use in ultrasupercritical steam power plants have shown that the alloy exhibited excellent resistance to oxidation in moist air (3% H₂O) over the 650-800°C (1200-1470°F) temperature range [8]. It was judged to have better oxidation resistance than 263, 617 and 740 alloy which were included in the test program.

The oxidation resistance of HAYNES 282 alloy is in line with other gamma-prime strengthened alloys such as 263 alloy and WASPALOY alloy. This is seen in Table 2 where the results oxidation studies in both air and air + 10% water vapor at 871°C (1600°F) are given [9-10]. In both environments 282 alloy was found to have comparable oxidation resistance to the other two alloys. These three alloys also performed similarly to each other in air + 10% water vapor at the lower temperature of 760°C (1400°F) [10]. These results are encouraging for 282 alloy in USC applications, since 263 alloy has been shown to possess excellent resistance to steam oxidation at 650°C (1200°F) and 800°C (1470°F) [11].

Table 2. Oxidation resistance of age-hardened alloys at 871°C (1600°F), 1008h exposure.

Alloy	Air		Air + 10% H ₂ O	
	Metal Loss (μm)	Avg. Metal Affected (μm)	Metal Loss (μm)	Avg. Metal Affected (μm)
282	5	35	2	31
263	3	46	3	36
WASPALLOY	8	44	2	37

5. Conclusions

The realization of advanced ultrasupercritical steam fossil power plants will require the use of special nickel-base alloys. Both HAYNES 230 and 282 alloys are prime candidates for such service because they satisfy the main material requirements. HAYNES 230 alloy has been included in the materials evaluation efforts, and investigation of the properties of the alloy is ongoing. HAYNES 282 alloy represents a new material that has high temperature strength capabilities beyond those of 740 alloy, which has previously been touted as having the highest strength capabilities. In addition to its creep strength, its fatigue resistance, oxidation resistance, and excellent fabrication characteristics make it a very attractive candidate. Therefore, it is believed that a serious effort should be undertaken to thoroughly evaluate 282 alloy for use in ultrasupercritical steam power plants.

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