Nickel-Base Furnace Alloy Extends Maximum-Use Temperature

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A new high-nickel furnace alloy offers the benefit of long-term operation at temperatures to 2200°F (1205°C), eliminating the erratic component life often associated with traditional heat-resistant materials at these extreme temperatures.

Materials used for thermal processing equipment and furnace fixtures must withstand increasingly harsh conditions including operating temperatures to 2200°F (1205°C). Add to that cyclical heating and aggressive environments, and traditional heat-resistant alloys often do not have the properties necessary to deliver the equipment life that users expect. RA 602 CA™ (UNS N06025) offers a good combination of properties at extreme temperatures to meet service life expectations.

All high temperature alloys have certain limitations. Material selection often is a result of compromises among many factors such as creep strength, maximum design temperature, environmental factors, ease of fabrication and repair, cost effectiveness and material availability. The chemical compositions of several common heat-resistant alloys are given in Table 1, and the effects of various alloying elements on material performance are shown in Table 2.

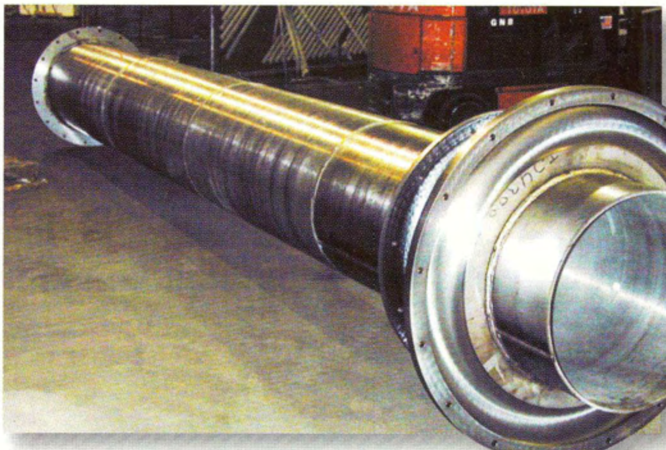
Although many of the alloys listed have been used at extreme temperatures, few have the combination of properties necessary for reliable operation at temperatures to 2200°F. Three problems that commonly contribute to the premature failure of alloys components operating in the 1800 to 2200°F (980 to 1205°C) temperature range are:

- Thinning or perforation caused by corrosion in the form of oxidation or other forms of chemical attack
- Deformation resulting from insufficient high temperature strength
- Fracture due to loss of toughness from grain growth and/or environmental factors such as carburization

These issues were addressed in the development of the new alloy.

Oxidation

The rate of oxidation or scaling for alloy components from oxidation increases with increasing temperature. Figure 1 illustrates the behavior of several heat-resistant alloys in cyclic oxidation tests at different temperatures and test times. Heat-resisting alloys rely on the formation of a thin, tightly adherent oxide scale for oxidation resistance. This layer acts as a barrier, which dramatically reduces the susceptibility of the alloy to further corrosion in the form of scaling. Chromium is the element most commonly used to impart scaling resistance. In sufficient quantities (> 12%), chromium reacts to form a continuous chromium-



Heat-resistant alloy RA 602 CA provides the required scaling resistance and creep strength for calciner used to process metal oxides.

Table 1 Nominal chemical composition of common heat-resistant alloys

	Content, wt%					
	Fe	Ni	Cr	Si	C	Other
AISI 309	62	13	23	0.8	0.05	
AISI 310	52	20	25	0.5	0.05	
RA 253 MA®	65	11	21	1.7	0.08	N, Ce
Alloy 800HT®	45	31	21	0.4	0.06	Al, Ti
RA 330 alloy®	43	35	19	1.25	0.05	
RA 353 MA®	36	35	25	1.2	0.05	N, Ce
RA 333®	18	45	25	1.0	0.05	W, Co, Mo
Alloy 617	1.5	54	22	0.03	0.08	1.0 Al, Ti
Alloy 230®	3	57	22	0.4	0.10	14W, Co, Mo. La
Alloy 214™	3	75	16	0.2	0.05	4.5Al, Y, Zr
Alloy 601	14	61.5	22.5	0.2	0.05	1.4Al
Alloy 600	8	76	15.5	0.2	0.08	
RA 602 CA	9.5	63	25		0.18	2.2Al, Y, Zr, Ti

Table 2 Effects of Alloying Elements of High-Temperature Alloy Performance

Element	
Nickel	Strength, carburization resistance, structural stability, ductility
Chromium	Oxidation resistance, strength
Aluminum	Oxidation resistance
Silicon	Carburization and oxidation resistance
Rare earths: cerium, yttrium, lanthanum	Oxidation resistance scaling
Molybdenum	Strength, weldability
Cobalt	Strength
Tungsten	Strength
Carbon	Strength
Nitrogen	Strength
Manganese	Weldability
Zirconium	Strength, grain-growth control

Source: Ref 1.

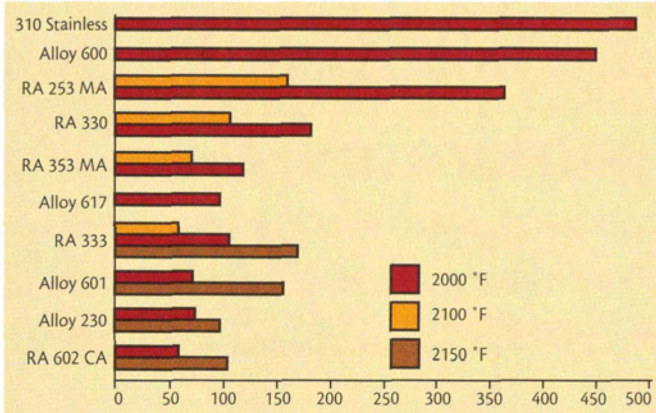


Fig 1 Oxidation rates for selected heat-resistant alloys at temperatures between 2000 and 2150°F. Samples were cycled weekly to room temperature over a test period of 1,500 to 3,400 hours. Source: Ref 2, 3.

oxide layer on the alloy surface. Typical chromium content of wrought heat-resistant alloys ranges from 15 to 25%.

Alloying with additional small quantities of rare-earth elements (microalloying) has enhanced the stability of this chromium oxide scale[4]. Cerium, yttrium and lanthanum are the more commonly used elements. Such alloying additions are becoming more common and are present in recent alloy developments. Aluminum and silicon additions improve scaling resistance by forming continuous alumina and silica sublayers below the chromium-oxide scale. These sublayers provide additional levels of protection between the atmosphere and the alloy.

Scaling resistance of RA 602 CA, even at extreme temperatures, is attributed to its high chromium content (25%) enhanced by additions of 2.2% aluminum and 0.1% yttrium. The aluminum addition allows for the formation of a continuous homogenous self-repairing Al_2O_3 subscale, and the addition of yttrium enhances the adhesion of the chromium and aluminum oxide layers.

Another measure of oxidation resistance is the amount of metal affected by internal oxidation and actual metal loss. Oxidation metrics are illustrated in Fig. 2. The appearance of RA 602 CA and Alloy 601 after 3150 hours at a temperature of 2100°F (1150°C) are shown in Fig. 3. Internal oxidation is prevalent in the alloy 601 sample, while only a thin oxide scale formed on the RA 602 CA surface. Freedom from internal attack is important in applications using sheet material, such as radiant tubes. Absence of internal oxidation means a greater percentage of the wall thickness is sound metal. As a result, the alloy retains a greater level of mechanical integrity. A comparison of oxide penetration in selected alloys is provided in Table 3.

Creep-rupture strength

Metals behave differently at high temperatures than they do near room temperature. Loading a metal bar to just below its yield strength at room temperature will not lead to failure or deformation regardless of the amount of time the stress is applied. At temperatures above 1000°F (540°C) and higher, mechanical strength is no longer independent of time. A metal component stressed to just below its yield point at red heat (1500°F, or 815°C, for example) will creep (stretch) slowly over time. Depending on the alloy, the stress level and the temperature involved, the component could last for hours, weeks or years until the metal finally fractures or ruptures. Because of creep, an alloy component can deform even under the stresses

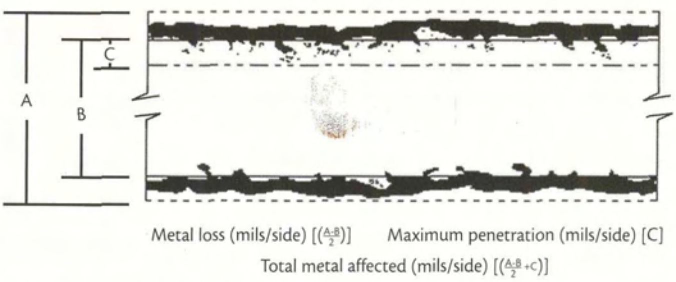


Fig 2 High-temperature oxidation metrics

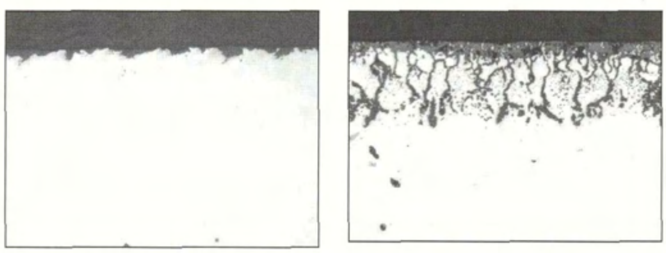


Fig 3 Surfaces of RA 602 CA (left) and Alloy 601 (right) after 3,150 hours exposure at 2100°F.

imposed by supporting its own weight. For this reason, the creep rupture strength is an important design criterion for any alloy intended for use above 1000°F.

The creep rupture properties of heat resisting alloys are heavily dependent on alloy content and grain size. In the case of RA 602 CA, its high creep-rupture strength primarily is a result of alloy content[5]. The relatively high carbon level ensures the precipitation of homogeneously distributed bulky carbides. Additions of titanium and zirconium ensure that these carbides and also carbonitrides are finely dispersed. Even solution annealing at 2230°F (1220°C) does not dissolve the carbides completely. Thus, the alloy achieves its high creep rupture properties from a combination of solid-solution hardening and carbide strengthening. The result is an alloy having greater creep-rupture properties than traditional alloys such as RA330 and alloy 601 (Tables 4 and 5). Further comparison indicates that at extreme temperatures, RA 602 CA compares favorably to other heat-resistant superalloys such as Alloy 214 and Alloy 230 (Table 6).

Grain growth

Brittle fracture of components exposed to extreme temperatures is a common occurrence. Operating at temperatures near or exceeding 1800°F (980°C) will lead to grain growth. A very coarse grain structure negatively affects alloy performance in several ways. Reduced resistance to thermal fatigue under cyclic conditions can cause cracking and fracturing. Susceptibility to corrosive mechanisms that preferentially attack at the grain boundaries also is increased. Such mechanisms include carburization, molten chloride-salt attack and corrosion by halogens. The attack is accelerated due to the reduced grain boundary volume and the more direct path into the alloy from the surface. Such types of attack reduce ductility. Often, the result is a component prone to brittle fracture. An example of such a failure is shown in Figure 4.

A small addition (approximately 0.08%) of zirconium in RA 602 CA is effective in pinning grain boundaries, thus greatly slowing the rate of grain growth[9]. The results of a recent grain growth study are detailed in Table 7. The information compares the grain growth of several heat-resistant alloys that are commonly used at temperatures above 1900°F (1040°C). The data was compiled from intermittent exposure of mill-annealed sample coupons to a temperature of 2050°F (1120°C) for a total of 990 hours.

Further evidence of the grain-growth resistance of RA 602 CA came from the examination of samples used in earlier cyclic oxidation testing. After exposure to 2100°F (1150°C) for 3,400 hours and 2150°F (1180°C) for more than 1,500 hours, the grain size only changed from ASTM 7 to ASTM 5.5 in both cases. In contrast, the grain size of alloy 601 exposed in the same tests increased to greater than ASTM 00.

The pick up of carbon from high temperature atmospheres is another potential reason for an alloy to lose its ductility during service. Table 8 compares the carburization resistance of several heat resistant alloys.

Conclusions

Higher operating temperatures can optimize many processes by increasing production, enhancing properties and improving the quality of parts being heat treated. The properties of traditional heat-resistant materials have limited furnace operators to

Table 3 High-temperature internal oxidation of some heat-resistant alloys

	Temperature, °F 2000		2100		2150	
	Time, h	Pene., mil	Time, h	Pene., mil	Time, h	Pene., mil
RA 330	3012	8.1				
Alloy 556	3012	3.8				
RA 333	3012	3.3	3000	9.8		
RA 353 MA	3012	9.7	3400	16.8	1500	13.1
800HT			3400	54.4		
RA 601			3400	7.6	1500	5.8
Alloy 214			3000	0.9		
RA 602 CA			3000	1.4	1500	3.2
Alloy 230			3000	6.3	1500	3.1
Alloy 617			3000	5.9		
AISI 446 Stainless steel			3000	78.1		

Table 4 Average stress to rupture in 10,000 h

	Stress, psi Temperature, °F 1400	1600	1800	2000	2200
RA 602 CA	11,300	3,200	1,490	670	240
Alloy 601	6,000	2,700	1,100	600	
RA 330	4,300	1,700	630	290(a)	140(a)

(a) Extrapolated. Source: Ref 6.

Table 5 Average stress for 1% creep in 1,000 h

	Stress, psi Temperature, °F 1400	1600	1800	2000	2100
RA 602 CA	9,400	2,380	960	330	140
Alloy 601		1,300	700	280(a)	
RA 330	3,600	1,700	220		

(a) Extrapolated

Table 6 Average stress to rupture in 1,000 h

	Stress, psi Temperature, °F 1800	1900	2000	2100
RA 602 CA	2,300	1,700	1,250	670
Alloy 230	3,000	1,800	1,000	600
Alloy 214	1,700	1,200	920(a)	

(a) Extrapolated. Source: Ref 7,8.

Fig 4 Fracture surface of a failed Alloy 600 thermocouple sheath taken from a molten-salt pot operating at temperatures in excess of 2100°F. Extensive grain growth has occurred due to overheating.

the choices of living with erratic alloy component life or reducing process temperatures. The new alloy offers the possibility of long-term operation at temperatures to 2200°F (1205°C) without compromise.

Table 7 Effects of exposure at 2050°F on heat-resistant alloy grain size

	ASTM average grain size						
Time, h	RA602CA	RA601	601GC	RA330	RA353MA	RA333	RA600
0	7	5	5.5	7	6	4	8
2	7	5	5.5	3.5	4	4	4
24	7	1.5	5	3.5	3	3.5	1
72	7	1	5	3	2.5	3	0
184	6.5	1	3.5	3	2.5	2.5	0
344	6.5	0	3.5	2.5	2	2	0
510	6.5	0	3	2	2	2	00
670	6.5	00	3	2	1.5	2	00
830	6.5	00	3	2	1.5	2	00
990	6.5	00	2.5	1.5	1.5	1	00

Table 8 Cyclic carburization resistance in a CH_4/H_2 environment(a)

	Weight change, mg/m²h		
	Temperature, °F (°C)		
	1380 (750)	1560 (850)	1830 (1000)
AISI 310 stainless steel	2	130	305
Alloy 800H	4	143	339
Alloy 601	2	69	152
RA 602 CA	0	44	58

(a) Ac = 0.8. Source: Ref 10.

Trademarks: 602 CA is trademark of Krupp VDM Technologies; 253 MA and 353 MA are trademarks of Avesta-Polarit; RA330 and RA333 are registered trademarks of Rolled Alloys; 800HT is a registered trademark of Special Metals Corp.; 230 is a registered trademark of Haynes International and 214 is a trademark of Haynes International. **IH**

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