Paper No. 05423 CORROSION2005

CASE HISTORIES ON SUCCESSFUL APPLICATIONS OF ALLOY 602CA, UNS N06025 IN HIGH TEMPERATURE ENVIRONMENTS

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ABSTRACT

Carbon steel, a workhorse of many industries, loses its usefulness above 538°C (1000°F) both due to strength degradation and corrosion. Alloy steels with chromium and molybdenum additions have expanded the useful temperature range of high temperature applications. However, with the increasing severity of high temperature environments encountered in modern day industries, there has been a singular lack of alloys, which can provide a combination of properties such as good mechanical strength and high temperature corrosion resistance to various modes of degradation (oxidation, carburization, metal dusting, etc.) up to 1200°C. This paper describes the development of one such nickel base alloy – alloy 602CA (UNS N06025) , which has provided a unique combination of properties by optimization of various alloying elements. This alloy since its introduction to the market in the early 1990's , has found numerous applications in the heat treat industry, annealing furnaces, furnace rolls, furnace belts, heat treat baskets, hydrogen reformer by-pass ducts, chemical vapor deposition retorts, serpentine grids, direct reduction of iron-ore technology to produce sponge-iron, calciners to produce very high purity alumina, calciners for chrome-iron ore for producing ferro-chrome, calciners to reclaim spent nickel catalysts, catalytic converters and glow plugs in the automotive industry, refineries, petrochemical industries, nuclear waste vitrification processes and many others. A brief description of some of these applications is presented in this paper.

Keywords: Alloy 602CA, UNS N06025, applications, high temperature, corrosion resistance, oxidation, carburization, metal dusting, high temperature strength, creep, stress – rupture

INTRODUCTION

Most high temperature nickel base alloys have sufficient amounts of chromium with addition of either aluminum or silicon to form protective oxide scales for resisting high temperature corrosion. Optimization of the various alloying elements led to a new alloy for service temperatures up to 1200°C in various industries. This alloy known as Nicrofer® 6025HT (alloy 602CA – UNS N06025) employs the beneficial effects of high chromium, high aluminum, high carbon and micro alloying with titanium, zirconium and yttrium. Developed in the early 1990's, the alloy has found numerous applications in various industries as mentioned above.

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The typical chemical composition of the alloy in weight % is given below:

Ni	Cr	Fe	Al	C	Ti	Zr	Y
Bal	25	9.5	2.2	0.18	0.15	0.06	0.08

This alloy is covered in ASTM, ASME via code case # 2359-1 to 1800°F for SC VIII, Div 1 use and SC 1 use for steam service up to 1650°F and other international specifications. AWS coverage has been approved for inclusion in AWS A5.11 (EniCrFe-12) for coated electrodes and A5.14 (ERNiCrFe-12) for bare filler wire.

The major beneficial features of this alloy are:

- Excellent oxidation resistance up to 1200°C, superior to other wrought nickel base alloys currently available in the market
- Good high temperature strength (stress rupture and stress to produce 1% creep at temperatures up to 1200°C), superior to many other Ni-base alloys over 1000°C.
- Excellent carburization resistance.
- Excellent metal dusting resistance.
- Excellent grain growth resistance

A brief recap of its physical metallurgy, high temperature degradation resistance, strength (stress-rupture, creep, tensile) and fabricability is presented with major emphasis on applications. Further details and data have already been published and are available in the open literature. Information on the original R&D development goals for this alloy, effects of the various alloying elements, physical metallurgy and micro-structural aspects are well documented in the various references. (1-9)

ALLOY 602CA DEVELOPMENT GOALS AND PROPERTIES

It is a well known fact that all high temperature materials and alloys have certain limitations and the optimum choice is often a compromise between various factors such as (1) the mechanical constraints and compatibility at maximum temperature of operation; (2) environmental constraints as imposed by the process conditions of high temperature, (3) ease of fabricability and repair, and (4) cost effectiveness and availability. Table 1 gives the typical chemical composition of several common high temperature alloys in commercial use today. However, there is a singular lack of an alloy possessing the combination of required properties (high temperature strength, high temperature corrosion resistance, ease of fabricability, cost effectiveness) for application up to 1200°C. Alloy 602CA appears to fulfill this void as proven by the various applications shown below in this paper.

TABLE 1
METALLURGICAL OPTIMIZATION OF ALLOY 602CA
NOMINAL CHEMISTRY COMPARISON TO SOME OTHER HIGH TEMPERATURE ALLOYS

Alloy	Fe	Ni	Cr	Si	C	Others
309	Bal	13	25	0.5	0.15	-
310	Bal	20	25	0.5	0.08	-
253MA	Bal	11	21	1.7	-	N ,Ce
330	Bal	35	19	1.25	0.05	-
333	18	45	25	1.0	0.05	C0 3 , W 3
800/800H	Bal	31	20	0.4	0.08	Ti, Al 0.4
45TM	23	Bal	27	2.7	0.08	RE
600	9	Bal	16	-	0.07	-
601	14	Bal	23	-	0.06	Al 1.4
602CA	**9.5**	**Bal**	**25**	**-**	**0.18**	**Y, Zr,Ti, Al 2.2**
214	2.5	Bal	16	0.10	0.03	Al 4.5, Y
X	18	Bal	22	-	0.10	W, Co, Mo 9
625	3	Bal	22	-	0.03	Cb 3.5, Mo 9
617	1.5	Bal	22	-	0.06	Co 12.5 , Mo 9, Al 1.2

TABLE 1 (continued)
METALLURGICAL OPTIMIZATION OF ALLOY 602CA
NOMINAL CHEMISTRY COMPARISON TO SOME OTHER HIGH TEMPERATURE ALLOYS

Alloy	Fe	Ni	Cr	Si	C	Others
188	1.5	22	22	0.3	0.10	W 14 , La 0.04
230	1.5	Bal	22	0.4	0.10	W 14 , Mo 1.2
120	Bal	37	25	0.6	0.05	Cb 0.7 , N 0.2
C4	2.0	Bal	16	0.04	0.005	Mo 16 , Ti 0.4
160	1.5	Bal	28	2.75	0.05	Co 29
690	9.0	Bal	29	0.20	0.02	----

Alloy 602CA Metallurgy

Alloy 602CA employs the beneficial effects of high chromium, high aluminum, high carbon and microalloying with titanium, zirconium and yttrium in a nickel matrix. The relatively high carbon content of approximately 0.18% to 0.2% in conjunction with 25% chromium ensures the precipitation of bulky homogeneously distributed carbides, typically 5 to 10 microns in size. Transmission and scanning electron microscopy suggest these bulky carbides to be of $M_{23}C_6$ type primary precipitates. Microalloying with titanium and zirconium allows the formation of finely distributed carbides and carbonitrides. Solution annealing even up to 1230°C does not lead to complete dissolution of these stable carbides and thus the alloy resists grain growth and maintains relatively high creep strength due to a combination of solid solution hardening and carbide strengthening [(9)] . This phenomenon of grain growth resistance is responsible for maintaining good ductility, a high creep strength up to 1200°C and superior low cycle fatigue strength. Repair and reconditioning of exposed parts is thus easily achieved. The presence of approximately 2.2% aluminum in this alloy allows the formation of a continuous homogenous self- repairing Al_2O_3 sub-layer beneath the Cr_2O_3 layer, which synergistically imparts excellent oxidation as well as carburization and metal dusting resistance; “Reactive elements” like yttrium significantly increase the adhesion and spalling resistance of the oxide layers, thereby further enhancing the high temperature corrosion resistant properties. Also, because of its relatively low aluminum content, this alloy does not embrittle due to gamma prime formation, as is the case with higher aluminum containing nickel alloys.

High Temperature Mechanical Properties

The mechanical properties of interest in designing high -temperature components are “time independent properties”, short term tensile (typically below 600°C) and “time dependent properties” (typically above 600°C), such as stress rupture and creep strength, and thermal stability i.e. maintenance of reasonable impact toughness after long aging. Table 2 lists some of these properties from recent production heats. Comparison with other high temperature alloys is provided elsewhere [(2)]. Table 3 lists the impact strength after aging at various temperatures up to 8000 hours. It is evident that alloy 602CA possesses adequate toughness properties for most industrial applications.

TABLE 2
HIGH TEMPERATURE MECHANICAL PROPERTIES OF ALLOY 602CA

Typical Short Term Tensile Properties

	Room Temp.	600°C	800°C	1000°C	1100°C	1200°C
UTS (KSI)	105	89	45	15.5	12	5
0.2% Y.S. (KSI)	51	38	35	13	9	4.5

100,000 hrs and 10,000 hrs Stress Rupture and 1%Creep Strength (KSI)

Temperature	R_m /10^{5}h	R_m/10^{4}h	R_p1.0/10^{5}h	R_p1.0/10^{4}h
650°C (1202°F)	18.8	24.6	16.7	21.0
700°C (1292°F)	13.0	17.4	10.87	14.8
800°C (1382°F)	3.62	5.1	1.74	2.9
900°C (1652°F)	1.67	2.46	0.81	1.36
950°C (1742°F)	1.23	1.74	0.55	0.94
1000°C (1832°F)	0.93	1.35	0.39	0.62
1050°C (1922°F)	0.68	1.09	0.25	0.43
1100°C (2012°F)	0.43	0.74	0.17	0.31
1150°C (2102°F)	0.33	0.58	-	0.20
1200°C (2192°F)	0.20	0.43	-	0.14

$R_m/10^5$h = Stress rupture in 100,000 hrs, $R_m/10^4$ h = Stress rupture in 10,000 hrs.
R_p. 1.0/10^5 = 1% creep in 100,000 hrs. R_p 1.0/10 ^{4} = 1 % creep in 10,000 hrs.

TABLE 3
IMPACT STRENGTH OF ALLOY 602CA IN J AFTER AGING
AT VARIOUS TEMPERATURES UP TO 8000 HOURS

Exposure Temperature And Condition	1000 Hrs.	4000 Hrs.	8000 Hrs.
Annealed Condition	Typical Values	78 to 84 J	
500°C Exposure	53	35	30
10% Cold Worked + aged	28	26	22
C.W.+ aged + Annealed	76	77	78
640°C Exposure	54	32	30
10% Cold Worked + aged	33	25	27
C.W.+ aged + Annealed	77	77	85
740°C Exposure	55	30	27
10% Cold Worked + aged	40	29	25
C.W.+ aged + Annealed	79	79	76
850°C Exposure	73	62	58
10%Cold Worked + aged	73	70	68
C.W.+ aged + Annealed	76	84	80

High Temperature Corrosion Resistance:

Oxidation:

It is well known that elements having greater thermodynamic affinity for oxygen tend for form passive barriers in alloy systems, thus providing the required resistance. Chromium, aluminum and silicon are the three major elements, which account for these passive barriers. The usefulness of protective chromia Cr_2O_3 is limited to around 950°C due to the formation of volatile chromium oxide (CrO_3). The higher thermodynamic stability of the alumina sub-layer, at even very low partial pressures of oxygen, improves the alloy 602CA oxidation resistance in cyclic tests. Rare earth elements further reduce the cracking, fissuring and spalling of the protective oxide alumina sub-layers.

Table 4 presents the laboratory test data on cyclic oxidation testing (24 hrs cycles – 1.5 hr heat up, 16 hrs hold at temperature, furnace cool down for test temperatures up to 1100°C, and cooling in air for temperatures higher than 1100°C) for periods up to 1200 hrs. As is evident, alloy 602CA gave superior performance when compared to many other iron-, nickel- and cobalt- based alloys. Metallographic examination of alloy 602CA showed a continuous alumina sub-layer without any selective internal oxidation by comparison to alloy 601 (Figure 1) The higher thermodynamic stability and more than five orders of magnitude lower dissociation pressure of alumina are the primary reasons for formation of the protective alumina layers.

TABLE 4
CYCLIC OXIDATION DATA – 1200 HOURS – 24 HR. CYCLES
WEIGHT CHANGE (mg / m^2h)

Alloy	750°C	850°C	1000°C	1100°C	1200°C
602CA	+0.4	+3	+12	+7	-310
X	+1	+8	+5	-5	-
800H	+7	+8	-24	-162	-
625	+1	+6	-100	-1410	-
601	+1	+10	+7	-24	-820
188	+1	+4	+7	-302	-
617	+4	+12	+19	-19	-

Metallographic examination of alloy 602CA showed a continuous alumina sub-layer without any selective internal oxidation by comparison to alloy 601. Further tests conducted on alloy 602CA and alloy 601 for 3,150 hours at a lower temperature of 2100°F (1148°C) again showed excessive internal oxidation with alloy 601. In contrast, alloy 602CA had no internal attack but only a thin surface oxide scale. This is especially beneficial in applications that utilize thin sheets such as in radiant tubes. No internal oxidation means the entire wall thickness is sound metal and the alloy retains most of its original properties. Another series of test at 2200° and 2250°F for 3040 hours show the excellent oxidation resistance of alloy 602CA at extreme temperatures. Other high creep strength alloys containing molybdenum (alloy 617) or tungsten (alloy 230) for strengthening showed extensive scaling in these tests. In the case of 617, the material had to be removed from the test due to the destruction of the 0.250 inch thick plate sample after one test cycle. Table 5 shows this data. The higher thermodynamic stability and more than five orders of magnitude lower dissociation pressure of alumina are the primary reasons for formation of the protective alumina layers. Work by other authors [10] has also shown good oxidation resistance of alloy 602CA.

TABLE 5
WEIGHT GAIN OF VARIOUS ALLOYS AFTER 3,040 HOUR EXPOSURE
IN AIR AT 2200°F (1205°C) & 2250°F (1232°C)

Alloy	2200°F (1205°C) Exposure Weight Gain (mg/cm^2)	2250°F (1232°C) Exposure Weight Gain (mg/cm^2)
602 CA	**47.6**	**61.8**
600	453.4	332.9
601	114.	138
214	----	21.9
230	348.3	----
353MA	231.9	323.8
333	155.6	-----
617	-----	327.63
		(617 removed after <200 hours)

Another series of cyclic oxidation test at 2100°F (1148°C) for 3,000 hours (cycle time of 160 hours) measured the weight loss as well as total penetration in mils by metallographic examination. These results are shown in Table 6 below. Again alloy 602CA gave excellent performance in these tests.

TABLE 6
WEIGHT GAIN AND INTERNAL PENETRATION OF VARIOUS ALLOYS
AFTER 3,150 HOUR EXPOSURE IN AIR AT 2100°F (1148°C)

Alloy	Weight Gain (mg/cm^2)	Max Internal Penetration (mils)
330	55	----
333	34	15.4
446 Stainless	>530	79.6
353MA	37	16.8
617	30	6.3
230	23	5.0
602CA	**18**	**1.4**
214	9	2.8
HR120	206	46.3
800HT	294	54.4

Carburization/Metal Dusting

Besides oxygen attack, high- temperature alloys are frequently subjected to attack by carbon. The degradation of metallic systems in carburizing environments can take two forms, namely carburization and metal dusting (some times referred to as catastrophic carburization). Metal dusting is a kind of corrosion, which manifests itself as pits and which proceeds at a rapid metal wastage rate at approximately 500-800°C in media with carbon activities significantly greater than one. Investigations by Grabke et al [(4,8, 9)] over a period of 10,000 hours showed that in contrast to the materials currently in common use, such as alloy 601 and alloy 600, the new alloy 602CA exhibited no metal dusting and had very good corrosion resistance under the applicable test conditions after 10,000 hours.

Due to the very low solubility of carbon in nickel, materials with high nickel content are considered beneficial for imparting carburization resistance. Alloys high in chromium, aluminum and silicon form a protective oxide layer, which prevents the ingress of carbonaceous corrosive species thus providing improved resistance. However, if alternating exposure to carburizing and oxidizing environments is experienced, the precipitated carbides are converted to oxides and the liberated CO widens the grain boundaries thus loosening the oxide layer, whereby causing accelerated deterioration.

The higher nickel plus chromium coupled with high aluminum content of alloy 602CA results in lowest weight gain in the temperature range tested as shown in Table 6. The reason for improved carburization behavior is due to the formation of an alumina sub-layer rather than via the nickel content alone as exhibited by the oxidation data in Table 4 at 1200°C for alloy 602CA and alloy 601.

In a recent study on metal dusting behavior of nine nickel base alloys and four Fe-Ni-Cr alloys [(4)] tested in a carburizing H_2-CO-H_20 gas with carbon activity $a_c > >1$ at 650°C, alloy 602CA was one of the most resistant material. Figure 2 shows the metal wastage rate of three nickel base alloys due to metal dusting. Table 7 gives the tabular data for the various materials tested. One very important point to note is that these results were obtained on unstressed coupons. In the real world the components exposed to metal-dusting type environments are stressed and hence have certain amount of strain. Alloy 602CA, even with 1% strain maintained its passive oxide layers thus preventing any accelerated attack whereas in alloy 690, the passive layer is damaged leading to accelerated metal wastage.

TABLE 6
CYCLIC CARBURIZATION BEHAVIOUR IN CH_4 / H_2 ENVIRONMENT (Ac = 0.8)
IN TEMPERATURE RANGE 750°C – 1000°C
Weight change (mg/m^2h)

Alloy	750°C	850°C	1000°C
310	2	130	305
800H	4	143	339
625	4	105	204

TABLE 6 (continued)
CYCLIC CARBURIZATION BEHAVIOUR IN CH_4 / H_2 ENVIRONMENT (Ac = 0.8)
IN TEMPERATURE RANGE 750°C – 1000°C
Weight change (mg/m^2h)

Alloy	750°C	850°C	1000°C
617	2	50	64
X	2	93	204
601	2	69	152
602CA	0	44	58

TABLE 7
TOTAL EXPOSURE TIME & FINAL WASTAGE RATE AFTER EXPOSURE IN METAL DUSTING ENVIRONMENT (CO- H2-H2O GAS AT 650°C)

Alloy	Surface Condition	Total Exposure Time in hours	Final Metal Wastage Rate in mg/cm^2h
800H	ground	95	0.21
HK-40	-	190	0.04
HP-40	-	190	0.038
DS	ground	1988	4.3×10^{-3}
600H	ground	5000	0.003
601	black	6697	7.3×10^{-3}
601	polished	1988	4.9×10^{-3}
601	ground	10000	5.8×10^{-4}
C-4	ground	10000	1.1×10^{-3}
214	ground	9665[1)]	1.2×10^{-3}
160	ground	9665[1)]	6.3×10^{-4}
45TM	black	10000	1.0×10^{-5}
602CA	black	10000	1.1×10^{-5}
617[2)]	ground	7000[1)]	3.7×10^{-6}
690	ground	10000	2.0×10^{-6}

[1)] The total exposure time of these specimens was less than 10,000 hrs., because they were inserted later than the other alloys.

[2)] Alloy 617 showed evidence of metal dusting after 7,000 hrs.

Other metal dusting tests conducted at Argonne National Labs under United States Department of Energy contract, again confirmed the excellent metal dusting resistance of alloy 602CA [(11)].

The combination of excellent high temperature strength at temperatures greater than 1000°C, and the excellent oxidation resistance up to 1200°C with good carburization/metal dusting resistance led to the selection and good performance of alloy 602CA in several diverse applications, as described below.

FABRICABILITY / WELDABILITY

Welding of alloy 602CA follows the same general rules established for welding other highly alloyed nickel base materials, where cleanliness is very important and critical [(2)]. Heat input should be kept low with inter-pass temperatures not exceeding 150°C, preferably 120°C. The use of GTAW process and matching filler metal is recommended. For shielded metal arc welding matching electrodes are available. Submerged arc welding with a GTAW top layer has also been successfully used. Preheating is not required. The shielding gas for GTAW is Argon + 2% Nitrogen and its use is very critical in preventing any hot cracking during Gas Tungsten Arc welding. For GMAW, the shielding gas is Argon with additions of helium, nitrogen and carbon dioxide (Argon + 5% Nitrogen + 5% Helium + 0.05% Carbon dioxide). Details on welding parameters, hot working, cold working, heat-treatment, de-scaling and machining are presented elsewhere [2, 12].

APPLICATIONS OF ALLOY 602CA

Due to the unique combination of the properties mentioned above, alloy 602CA has been extensively used in the following applications.

- Heat Treat Industry: Chemical vapor deposition (CVD) furnaces, vacuum furnace fixtures, furnace rolls, bell furnaces, bright annealing muffles, accessories and transport hooks for enameling furnaces, transport rollers for ceramic kilns, wire conveyor belts, anchor pins for refractories, bar frame baskets, burner components, serpentine grids and other furnace accessories.
- Calciners: Rotary kilns for calcining and production of high purity alumina, calcining of chromic iron ores to produce ferro-chrome, cobalt, copper and nickel oxide calciner, reclamation of spent nickel catalysts from petrochemical industries
- Chemical/Petrochemical - Production of hydrogen via a new steam reformer technology
  - Production of phenol from benzene via a new and cheaper process
  - Pig Tails in refinery reformers
  - By-pass ducts in waste heat boilers in ammonia and methanol synthesis
  -
- Automotive – catalytic support systems, glow plugs, exhaust gas flaps
- Vitrification of nuclear waste
- Direct reduced iron ore technology to produce sponge iron.

A brief description of some of these applications is given below:

STEEL MILLS

Furnace Rolls: The industry's search for "new material" furnace rolls used in annealing of hot/cold rolled plates of nickel, nickel alloys and stainless steels, intensified once asbestos-lined water cooled carbon steel/low alloy steel furnace rolls were prohibited due to the carcinogenous nature of asbestos. Cast metallic rolls of nigh nickel alloys and Nickel Aluminide and others have also been used by the industry with mixed success. The major problem has been pick up from the rolls on the bottom side of annealed sheets (1 mm to 3 mm thick) and plates leading to extensive rework or scrapping of these finished products altogether – a very costly and expensive proposition.

Also in many cases, these rolls required very frequent grinding to prevent roll pick up on the bottom of annealed sheets, again a significant cost item. For grinding of the rolls sometimes on a weekly basis, the furnace had to be shut down, cooled, rolls taken out of the furnace, maintenance grinding done and then re-installed and re-fired.. These frequent cooling/heating cycles also put additional stresses leading to reduced life of the furnace rolls.

Due to the above problems, the ThyssenKrupp VDM GmbH in 1993 installed a few rolls made from longitudinally welded plates of alloy 602CA in the annealing furnace. Based on the excellent results obtained with the first set of rolls installed in 1993/1994, all the 80 plus furnace rolls now have been replaced with alloy 602CA. Figures 3A & 3B show the overall view of the annealing furnace with the alloy 602CA furnace rolls. The operating temperature for the furnace rolls varies, between 700°C to 1200°C, depending on the alloy, being annealed. Use of alloy 602CA furnace rolls significantly reduced maintenance costs, energy costs, inspection costs of annealed products and contributed to improved profits by increased recovery of finished products. The payback period on this investment has been approximately two years.

Another major stainless steel company in mid-west USA was having serious maintenance problems with centrifugally cast rolls with frequent replacements. A trial run with four alloy 602CA furnace rolls provided significant savings, which could be utilized by replacing all the 62 rolls in their present annealing furnace. Other companies in the USA and in Europe are considering changing their furnace rolls with un-cooled alloy 602CA rolls.

Muffles: Muffles used for continuous bright annealing at a company in Hagen, Germany, required an increased operating temperature from 1150°C to 1200°C. After evaluating the properties of alloy 602CA, previous muffle material (X15CrNiSi25-20 – Material # 1.4841) was replaced with alloy 602CA. The furnace is 15 meters long and 1 meter in diameter and weighs about 12 tons. Even with the higher temperature, the first shortening of the muffle due to creep only became necessary after 18 months of service and now the dimensional stability has been maintained. In mid 1997 the world's largest suspended bright annealing furnace of alloy 602CA weighing more than 20 tons was installed at a company in Belgium. The first trial phase operation up to 1150°C was conducted satisfactorily. Figure 4A, B and C shows pictures of some of these muffles.

Argon Oxygen Decarburization (AOD) Chutes: Alloying additions are made in one U.S. stainless steel mill during the refining process performed in an AOD vessel. These alloying additions added by way of a chute shown in figure 5. The chute is made of ½ inch plate material and sets above the molten 400 series stainless steel, which would be at temperatures above 1427°C (2700°F). The chute sees significant radiant heat and based on metallography typically operates at a metal temperature of approximately 1260°C (2300°F). Chutes made of 310 stainless were replaced every 2-4 weeks. Chutes were made using alloys 353 MA and alloy 230. These extended the life to 6 weeks and 12 weeks, respectively. Alloy 602 CA has been lasting on average 16 weeks, which is a 33% increase in life over the more costly alloy 230.

HEAT TREAT INDUSTRY

Bell Furnaces for Annealing of Magnetic Cores: The alloy 602CA bell is externally heated in air, whilst the interior is under a 100% hydrogen protective atmosphere to prevent oxidation of the magnetic cores. These cores had to be annealed at a precise temperature of 1200°C minimum, to develop optimum magnetic properties. Hence it is necessary to heat the bell exterior to 1230°C. Due to this high temperature, the outer surface of bell has a rough texture with a grainy appearance, however, the dimensional stability and mechanical integrity of the bell has not been compromised. The furnace continues to operate satisfactorily.

Annealing Furnace for Gas Turbine Casing: The casings of land based gas turbine combustion chambers made from alloy 617 have to be annealed after a few years in service. This is necessary to redissolve the various precipitates (carbides, other phases) before any weld repair or maintenance can be done and also to restore the component to a proper micro-structural condition. This is done by annealing at 1120°C followed by forced air cooling. Due to the high creep rupture strength, outstanding oxidation resistance and thermal fatigue resistance, alloy 602CA was chosen for the annealing bell. The bell has performed flawlessly and met all the design conditions (Figure 6).

Chemical Vapor Deposition Retorts: Alloy 602CA has replaced alloy 600 at one gas turbine blade supplier for its chemical vapor deposition (CVD) retorts. An aluminide coating is applied to the turbine blades using the CVD process at approximately 1975°F, internal temperature. Since the alloy retort is externally heated, the wall temperature of the retort is likely 100-150°F higher than the process temperature. Due to a partial vacuum used in the process, external reinforcements in the form of belly bands are used to prevent collapse of the retort wall. The trial involved making five belly bands from alloy 602 CA (three bands) and alloy 600 (two bands) alternated (Figure 7). After nine months in service the strength and scaling resistance benefits of alloy 602 CA were evident. All current and future retorts are currently made entirely out of alloy 602 CA.

A second application was for an Aluminizing CVD coating retort for turbine blades. The unit replaced alloy 230 and was constructed out of 3/8" plate into a 30" diameter retort using GTAW welding process (shielding gas was 98%Ar+2% N_2). Alloy 602CA was selected for its cost effectiveness and excellent creep and spallation resistant properties.
Alloy 602 CA retorts 28 inches in diameter and 0.120 inches thick have replaced alloy 214 in aerospace coating operation. Due to the light gage used and the operating temperatures of 1900-2000°F, excellent scaling resistance is a necessity. Alloy 602 CA was chosen as the replacement based on increased creep-rupture properties, similar scaling resistance, and improved weldability.

Enameling Furnace Hardware: Hangers for enameling parts moving continuously through the oven must be heated from room temperature to 850 °C for the first time entering the oven; and for each subsequent operation these hangers must again be heated up from 600 to 850°C, the operating temperature of the furnace. Previously alloy 601 hangers were used. Due to the higher creep strength and superior oxidation resistance of alloy 602CA, a thinner cross-section hanger could be utilized, resulting in a weight savings of approximately 500 kg (25%) for all the hangers involved going through the oven at one time. This reduction equated to lower initial costs for the hangers and related driving train components. Energy costs were also lowered due to the lower mass of the hangers. Total operating costs were reduced by approximately $16,000 on an annual basis. Another major saving was due to lower rejection rate of the enameled parts due to the non-spallation characteristics of alloy 602CA hangers. Also elimination of distortion of alloy 602CA hangers provided for easier loading and un-loading of the furnace.

Transport Rollers for Ceramic Kilns: At operating temperatures of approximately 1150°C to1180°C alloy 602CA have already exceeded the service life of alloy 601, the current standard alloy for this application, with no indication of failure, in the foreseeable future. Alloy 602CA rolls are expected to provide a significant improvement in life over alloy 601 rolls.

Grids & Baskets: Alloy 602 CA has been used for vacuum furnace applications. The serpentine type grid shown in figure 8 was constructed out of alloy 602 CA, as an upgrade to alloy 330 (UNS N08330) for annealing large nickel superalloy castings. The tray was designed to carry loads from 700-2000# inside the furnace during heat treatment in the 2175 to 2260°F range followed by up to a 6 bar nitrogen quench. Alloy 602CA was selected for its superior high temperature strength, which kept the tray as light as possible. Lower fixture weight allows for faster heating and cooling and reduced energy consumption. To date the fixture has been in service for over two years and has withstood an estimated 2000 cycles.

Alloy 602CA is currently in trial in a low-pressure carburizing heat treat furnace at a captive heat treat shop. 12mm diameter Alloy 602CA round bar was used to construct the three bar frame baskets shown in figure 9 to be tested against alloy 330 for the case hardening of automotive transmission gears. The furnaces are an Abar Ipsen design and operate at 900°C (1652°F) followed by an integral oil quench. The carburizing gas is acetylene based. The baskets will see two cycles per day on average.

Wire Conveyor Belts: In a company in South Africa, alloy 601 belts for conveying a pelletized mixture of soda ash and zircon sand in a 24 meter long furnace operating at 1050°C failed in less than 4 weeks due to a combination of high temperature corrosion (oxidation, carburization) and mechanical stresses leading to stretching of the belt by creep. Replacement belts made from alloy 602CA wire (4.17 mm diameter) have already exceeded the life obtained with 601 belts.

Conveyor Belt in Heat Treating Furnace: Alloy 310SS belts used in a hardening furnace to transport carbon steel parts lasted only 4 months due to sigma phase formation and insufficient creep strength leading to lengthening of the belt and reduction in width. This caused the parts to fall of from the belt causing maintenance problems and rejection of the parts. By replacing the belt with alloy 602CA, the life was increased by a factor of 6 to 8 times.

Calciner for production of high purity alumina : Production of 99.99% purity alumina required calcining at high temperatures around 1200°C. With alloy 601 the maximum temperature limitation of 1150°C prevented achieving the high purity and also the life of the alloy 601 calciner was short. With alloy 602CA, calcining at 1200°C was made possible. The company is very satisfied with the performance of alloy 602CA calciner and are able to produce very fine (-325 mesh) alumina to the desired "purity and whiteness level". The fine alumina powder is used in many industrial and consumer products. Figure 10 shows the calciner and its internal hardware, all constructed out of alloy 602CA. After seven years of successful operation, a crack developed in this calciner due to overheating and malfunctioning of burners in one section. This was weld repaired and put back into service. This company has ordered another spare calciner tube measuring approximately 40-1/2 inches outside diameter and 30 feet long using 15mm (0.591 inch) thick plate.

Calciner for chrome iron ore: Calcining of chrome iron ore was carried out in a rotary kiln made from alloy 602CA, 1.83 meters in diameter x 13 meters long. There is a temperature gradient from 850°C to 1200°C, over the length of the kiln. Prior to constructing from alloy 602CA, corrosion tests were carried out in this medium where the alloy gave excellent performance. A rotary kiln is actually subjected to cyclical tension/compression stresses and since the resistance of alloy 602CA to cyclical tension/compression stress is markedly higher than the corresponding static creep rupture strength in the temperature range in question, a great deal of additional safety and service life was incorporated into the rotary kiln. This kiln has now been in service since 1994 and is giving excellent performance. Another particularly helpful feature for the use of alloy 602CA in components subjected to fatigue loading is the very low frequency dependence of the fatigue strength in the range 0.1 – 1Hz. This also enables the rotational speed of rotary kilns or furnace rollers to be changed without having to fear any failure due to any dramatic decrease in fatigue strength. This is a unique and very useful feature of alloy 602CA.

Calciner for reclaiming spent nickel catalyst: A major U.S. chemical company in their operation uses nickel catalysts. To reclaim the nickel after usage over a period of time, these have to be heated to 1200°C. Alloy 602CA was the only alloy, which provided the necessary combination of properties required for this calciner.

Cobalt, Copper & Nickel Oxide Calciner: Oxides of cobalt, copper and nickel of very high purity are used as color pigmentation in the manufacture of colored glass. Temperature of operation varies between 600 and 1100 °C. The starting product are salts of these elements in form of carbonates and/or hydroxides. Calcination yields fine oxides of Co, Ni and Cu which are then pulverized (ground) to oxide particles less than 5 to 10 microns in size. These oxides are used as color pigments for glass, electrical pole surge protectors, metal oxides in re-chargeable batteries and other applications. No contamination is permitted in these powders . Alloy 602CA was selected after testing due to its high temperature strength, oxidation and spallation resistance properties. Figure 11 shows a picture of this calciner.

CHEMICAL / PETROCHEMICAL / REFINERIES

Hydrogen Production: A major U.S. chemical company has developed a new steam reformer technology. To produce hydrogen, from methane, steam and a proprietary catalyst, at 1100°C. The process consists of transporting the process media through a centricast tube. To keep the centricast tube uniformly heated, so that no hot spots develop (thus increasing life of the tubes) and to facilitate maximum heat transfer, a shroud of 7 mm thick alloy 602CA was used over these centricast tubes, thus creating a "black box" environment. The heating flue gases pass in the annular space of the shroud and tubes thus keeping the tubes uniformly heated. Alloy 602CA was selected due to its excellent high temperature strength, oxidation resistance and metal dusting/carburization resistance.

Refinery: Pilot tests with alloy 602CA were conducted in refinery pig tail applications where metal dusting resistance is needed. The environment consisted of methane, CO, CO_2, propylene, and H_2. Alloy 310SS, 800H and the high silicon containing alloy RA85H did not perform well due to either embrittlement or severe metal dusting wastage. Alloy 310 failed by sigma phase formation. After 10,000 hours of operation, alloy 602CA had the lowest metal wastage of less than 0.005" compared to some other nickel alloys having wastage rates varying between 0.009" to 0.047". Alloy 600 had a wastage rate of 0.022", alloy 556 with a wastage of 0.036", alloy 230 at 0.022", alloy RA333 with a wastage rate of 0.047" and RA85H at 0.009". After 25,000 hrs alloy 602CA continues to give excellent service. Pilot tests with alloy 602CA in this refinery pig tail applications showed this alloy to potentially increase the current life from less than 2 years to about 6 to 8 years, a three to four fold increase [(8)].

Phenol Production: In another test program for a new technology to produce phenol from benzene, where metal dusting / carburization/is a serious problem, alloy 602CA is being tested along with other alloys. Preliminary results showed alloy 602CA to perform well.

Ammonia Plant (Europe): In a three year test program at temperatures 450 to 850°C, alloy 602CA had no metal dusting attack whereas alloy 601 had some attack and alloy 800H severe attack. This again confirms the laboratory tests conducted by Grabke et al. and others [(4,11)]. The plant selected alloy 602CA for the various components. In another plant in Western Europe, alloy 602CA showed no metal dusting (temperature and exposure time were not revealed).

Methanol Plant (Europe): Testing and usage with alloy 602CA and alloy 601 showed alloy 602CA to perform significantly better than alloy 601. No other details were given. The metal dusting results of Grabke et al. have been confirmed by other companies as well in the ammonia and methanol plants in Europe and USA. It has been postulated that increased efficiency of ammonia and methanol plants can only be achieved by decreasing the steam /carbon ratio, thus increasing higher carbon activity and consequently greater tendency to material wastage by metal dusting phenomenon.

Based on the success of alloy 602CA, many other tests programs with this alloy are underway in industry. Unfortunately, details are not available due to the confidentiality aspects of these tests being conducted by the various companies. One important emerging technology in the pilot R&D stage is the reforming of natural gas and other hydrocarbon fuels to produce hydrogen for use in fuel cells. Many companies are involved in testing and proving this technology and the produced hydrogen will then be used in fuel cells to power individual households with distributive power. In some of the initial testing, alloy 602CA has performed very well. However the details of these test programs are proprietary and confidential.

This alloy is also specified for a project in Australia / New Zealand in steam reforming units as used in methanol, ammonia and hydrogen production, where metal dusting is a serious problem. Another company in Norway after extensive testing (corrosion coupons were attached to the butterfly vanes of the by-pass valve) selected alloy 602CA in a Methanol plant for construction of a by-pass valve in the waste-heat boiler of the reforming section. Temperatures, ranging from 520 to 630° C, and the environment, has relatively low steam to carbon ratio.

DIRECT REDUCTION OF IRON ORE TECHNOLOGY

In direct reduction plants for iron ore and in the petrochemical industry, in plants for synthesis of hydrocarbons, methanol, ammonia, etc., a form of damage known as “metal dusting” is frequently observed. Metal dusting is a kind of corrosion, which manifests itself as pits, and which proceeds, at a rapid metal wastage rate at approx. 500-800°C in media with carbon activities significantly greater than one. Investigations by Grabke et al over a period of 10,000 hours showed that in contrast to the materials currently in common use, such as alloy 601 and alloy 600, the new alloy 602CA exhibited minimal metal dusting and had very good corrosion resistance under the applicable test conditions after 10,000 hours.

This was one of the reasons for the decision in 1996 (along with its excellent high temperature strength properties) to use this material in prefabricated sections up to 50 mm thick in a direct reduction plant operating according to the COREX process. The components fabricated from alloy 602CA have so far performed as designed.

NUCLEAR WASTE VITRIFICATION

Due to its excellent high temperature properties, alloy 602CA has been used for “Vitrification Pots” at Cogema in France. In these pots, Cogema glass is heated to 1150°C. Alloy 602CA continues to give good service since many years.

Studies done at the Westinghouse Savannah River Company [13] again confirmed the excellent behavior of alloy 602CA for use as the top head and off gas components in the Defense Waste Processing Facility (glass-smelter) at the Department of Energy’s Savannah River site.

OTHER APPLICATIONS

Pollution & Noise Control in Automobiles: To combat pollution, automobiles are equipped with catalytic converters. The catalyst support is typically made of an FeCrAl alloy, but in cases, where higher strength and appropriate oxidation resistance is needed, alloy 602CA is being used in thickness of 50 microns (0.002"). Recently, with improvements in rolling technology and the need to increase efficiency, thickness’ as low as 30 microns are being required.

In the middle of the 1990’s, exhaust flaps were tested for noise reduction in passenger cars. These components are very near the engine and hence see high temperatures and require ceramic sliding bearings as well as metallic materials. Alloy 602CA was selected after extensive testing for the shaft, bearing cover, lever arm and bearing box.

Burners: In a hazardous waste incinerator, alloy 625, C-276 and other alloys in the burner section, operating at 2000°F, used to fail by a combination of oxidation, carburization and chloridization attack in a relatively short time. Based on the coupon test program, this company has ordered pipes of alloy 602CA (1½” and 2 ½” sch 40) for trials.

Muffles: In a recent application, a captive heat-treatment company replaced alloy 230 with alloy 602CA muffle constructed out of 3/8” plate. The operating temperature will be around 1100°C (2000°F).

In another application two corrugated muffles for sintering (2050°F) of metal powder components in hydrogen atmosphere were constructed with alloy 602CA replacing alloy 601. Alloy 602CA was selected based on its higher strength, improved carburization resistance and resistance to grain growth. Alloy 601 muffles used to fail by cracking as a result of reduced ductility (grain growth and carburization caused by binders being burnt of the sintered parts). Corrugation process of alloy 602CA was achieved without any cracking. The welding process employed was GMAW using 0.045” welding wire. Shielding gas used was Argon + 5% Nitrogen + 5% Helium + 0.05% Carbon dioxide.

Retorts: Four horizontal box retorts were constructed out of 3/16" (7" tall x 15" wide x 17" deep) plate for stabilizing plutonium oxide for long term storage and possible use as nuclear fuel in future. TIG welding process was used in the construction. Alloy 602CA was selected over 601 due to its increased oxidation resistance and creep strength since the temperature of operation was to be approximately 1010°C (1850°F). The alloy 602 CA retorts operated for the two year length of the program with no operational issues.

Fuel Cells: Recently great interest has been generated in applications of fuel cells for residential power generation by reforming of natural gas and/or other hydrocarbons to produce hydrogen which is a key ingredient in this technology. In this reforming technology the alloy is exposed to methane, hydrogen, carbon dioxide, and carbon monoxide at temperatures varying between 850 and 1100°C. Alloy 602CA has been selected by a couple of companies after testing many commercial alloys in this technology. Pilot plant tests are under planning with alloy 602CA.

CONCLUSIONS

The industry demand for a reasonably priced material suitable for up to 1200°C, both mechanical property wise and high temperature corrosion resistance wise have been fulfilled by alloy 602CA as evidenced by the various applications described above. The cost effectiveness, availability and limits on use of heat treatment plants and industrial furnaces often depend on the capacity of material of construction at high temperature to posses adequate mechanical strength, good oxidation resistance, good carburization/metal dusting resistance, good thermal fatigue strength, good thermal stability and at the same time must be able to withstand cyclical thermal stresses. Alloy 602CA has this unique combination of properties.

The industrial experience gained has confirmed that alloy 602CA can be used without problems in heat treatment and industrial furnace engineering up to 1200°C and is a cost effective alternative to other alloys in resisting extremely aggressive corrosive conditions of metal dusting, carburization and high temperature oxidation as may be encountered in refineries, chemical and petrochemical industries. The various application pictures clearly prove the alloy's excellent fabric ability and weld ability characteristics.

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