# COMBATTING HIGH TEMPERATURE CORROSION WITH ALLOY 602CA (UNS N06025) IN VARIOUS ENVIRONMENTS AND INDUSTRIES

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### ABSTRACT

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 the mechanical constraints and compatibility at maximum temperature of operation, environmental constraints as imposed by the process conditions of high temperature, ease of fabricability and repair, cost-effectiveness and availability. Alloys designed to resist high temperature corrosion have existed since the beginning of the 20<sup>th</sup> century. 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 for high temperature applications. However, with the increasing severity of high temperature environments encountered in modern day industries, there has been a need for an alloy which can provide a combination of properties of both good mechanical strength as well as 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 an unique combination of properties by optimization of various alloying elements. Since its introduction to the market in the early 1990's, this alloy has found numerous applications in the heat treat industry, annealing furnaces, furnace rolls, furnace belts, 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, exhaust flaps 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 also presented in this paper.

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

## **INTRODUCTION**

For high temperature applications, nickel base alloys must posses a combination of high temperature strength as well as resistance to various modes of high temperature degradation. The strengthening could be achieved by solid solution hardening (Mo, W, Nb, Ti, Co, Ta Hf), precipitation hardening (Al + Ti, Al, Ti, Nb, Ta), dispersion or carbide/nitride hardening (Cr, Mo, W, Ti ,Zr, Ta, Nb) or a combination thereof. The high temperature corrosion resistance is achieved by formation of adherent spallation resistant (La, Ce, Y, Hf, Zr, Ta) oxides of chromia, alumina and/or silica. Most high

temperature alloys have sufficient amounts either of chromium with addition of either aluminum or silicon to form the protective oxide scales for resisting high temperature corrosion. Table 1 gives the typical chemical composition of several common high temperature alloys in commercial use today. 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 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. The typical chemical composition of the alloy in weight % is given below:

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

This alloy is covered in ASTM and other international specifications. ASME code case 2359 has been approved for SC VIII, Div. 1 and SC I (steam service only) up to 1650 °F. AWS coverage for weld filler metal in A5.11 and A5.14 is under progress.

The major properties of interest in 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 most other Ni-base alloys over 1000°C.
- Excellent carburization resistance.
- Excellent metal dusting resistance.

A brief recap of its physical metallurgy, high temperature degradation resistance, strength (stress-rupture, creep, tensile) and fabricability are 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.<sup>(1-9)</sup>

## **ALLOY 602CA DESCRIPTION & PROPERTIES**

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 (Figure 1). 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. 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. Figure 2A shows the brittle fracture of alloy 601 corrugated muffle furnace from the combination of excessive grain growth and carburization. In contrast Table 2 shows the grain growth data for various high temperature alloys where alloy 602CA had very little grain growth even after approximately 1000 hours of exposure at 2050°F (1121°C). Figure 2B shows that even after 3150 hours exposure at 2100°F (1148°C), the original grain size of ASTM 7 only increased to ASTM 5.5. Hence repair and reconditioning of exposed parts can easily be achieved with alloy 602CA. The presence of approximately 2.2% aluminum in this alloy allows the formation of a continuous homogenous self- repairing Al<sub>2</sub>O<sub>3</sub> sub-layer beneath the Cr<sub>2</sub>O<sub>3</sub> layer, which synergistically imparts excellent oxidation as well as carburization and metal dusting resistance; "Reactive elements" like yttrium significantly increase the adhesion and spallation 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. This alloy is available in twoconditions, the most common being Nicrofer® 6025HT (alloy 602CA), which is solution annealed at 1220°C with typical grain size greater than 70 microns and is used in those applications where both high temperature corrosion resistance and good stress rupture and creep properties are required. In special cases, where only the high temperature corrosion resistance is needed, this alloy is supplied in annealed condition of 1180°C with grain size less than 70 microns.

#### **High Temperature Mechanical Properties:**

The mechanical properties of interest in designing high -temperature components are "time independent properties", e.g. 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 3 lists some of the mechanical properties from recent production heats. Comparison with other high temperature alloys is provided elsewhere <sup>(2,7,8)</sup>. Recent work on determining 10,000 hours average rupture strength of alloys 330, 230 and 602CA are shown in Figure 3. As is evident from this figure, alloy 230 has higher creep rupture strength values in comparison to alloy 602CA below  $1800^{\circ}$ F but exhibits lower values above  $1800^{\circ}$ F<sup>(10)</sup>. Table 4 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.

#### High Temperature Corrosion Resistance:

<u>Oxidation</u>. 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<sub>3</sub>). The higher thermodynamic stability of the alumina sub-layer <sup>(11)</sup>, 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.

Table 5 presents the laboratory test data on cyclic oxidation testing (24 hrs cycles – 1.5 hr heat up, 16 hrs hold at temperature, and furnace cool down, for test temperatures up to 1100°C, and cooling in air for temperatures higher than 1100°C) for periods up to 1,200 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 4.) 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 (Figure 5). 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. 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 <sup>(12)</sup> have also shown good oxidation resistance of alloy 602CA. 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.

#### **Carburization/Metal Dusting**

Besides oxygen attack, high-temperature alloys are frequently subjected to attack by carbon. Gaseous environments generated by many high temperature industrial processes, particularly in the petrochemical/refinery industries, in the conversion of fossil fuels and in certain heat-treat operations, frequently contain gases with carbon activities of up to 1. In other cases such as in ammonia or methanol synthesis, carbon activities can be much higher than 1. The degradation of metallic systems in carburizing environments can take two forms, namely carburization and metal dusting (some times referred to as catastrophic carburization). 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 may form protective oxide layers, 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<sup>(14)</sup> thus loosening the oxide layer, thereby 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 7. 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 5 at 1200°C for alloy 602CA and alloy 601 and Table 6 data at 2100°F (1148°C). A recent study <sup>(13)</sup> by Brill and Agarwal, examines the carburization behavior of various nickel and iron base alloys in the temperature range of 550°C to 1200°C. The results from this study also confirm the excellent carburization resistance of alloy 602CA. Another paper by Brill <sup>(14)</sup> shows the mathematical relationship between the effects of the alloying elements in an alloy with the carburization resistance. Brill

introduced a constant  $K_B$  which showed the positive effect of Ni+Co, Mo, Si, Mn, Al and C. The higher the value of this constant, the better was the performance of the alloy in carburizing environments <sup>(13)</sup>.

In a recent study on metal dusting behavior of nine nickel base alloys and four Fe-Ni-Cr alloys<sup>(4, 9)</sup> tested in a carburizing  $H_2$ -CO- $H_2O$  gas with a carbon activity  $a_c > 1$  at 650°C, alloy 602CA was one of the most resistant material. Table 8 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 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. Fig. 6 shows the comparison between alloy 600, 601 and 602CA. Greater details on the subject of metal dusting is presented elsewhere <sup>(15)</sup>.

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 later.

## 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 <sup>(2)</sup>. 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 <sup>(2, 16)</sup>.

## **APPLICATIONS OF ALLOY 602CA**

Due to the unique combination of the above mentioned properties, alloy 602CA has been extensively used in the following applications. More potential applications continue to develop via test programs being conducted in many industries and will be reported in future as they materialize.

- Heat Treat Industry: Furnace rolls, bell furnaces, bright annealing furnaces, accessories and transport hooks for enameling furnaces, transport rollers for ceramic kilns, wire conveyor belts, anchor pins for refractories, tubes for bright annealing wires, and other furnace accessories.
- Calciners: Rotary kilns for calcining and production of high purity alumina, calcining of chromic iron ores to produce ferro-chrome and 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 reformer
- Automotive: catalytic support systems, glow plugs, exhaust gas flaps
- Nuclear Industry: vitrification of nuclear waste
- Metallurgy: Direct reduction of iron ore technology to produce sponge iron.

A detailed description of some of these applications along with pictures of the various components fabricated from alloy 602CA are presented in Corrosion/2000 paper # 521 and reference # 16. Some other recent applications are presented below.

#### **Recent Applications of alloy 602CA**

<u>Cobalt, Copper & Nickel Oxide Calciner</u>. 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 7 shows a picture of this calciner.

<u>Pollution & Noise Control in Automobiles.</u> 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.

<u>Burners.</u> 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 ( $1\frac{1}{2}$ " and  $2\frac{1}{2}$ " scd 40) for trials.

<u>Serpentine Grid.</u> In a vacuum furnace operating at 2200°F, alloy 230 was not giving sufficient life. The company is testing alloy 602CA in this application.

<u>Muffles.</u> 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 (  $2050^{\circ}$ 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.

<u>Retort.</u> The 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<sub>2</sub>). Alloy 602CA was selected for its cost effectiveness and excellent creep and spallation resistant properties.

In another application 4 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 between 1150°C and 1200°C (2100 to 2200 °F).

#### Applications in Chemical / Petrochemical / Refineries

<u>Hydrogen Production</u>. 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.

<u>Refinery.</u> 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<sub>2</sub>, propoleyne and H<sub>2</sub>. 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 15,000 hrs alloy 602CA continues to give excellent service.

<u>Phenol Production.</u> 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 <sup>(4,9,14)</sup>. 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).

<u>Methanol Plant (Europe)</u>. 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.

<u>Fuel Cells</u>. 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 to 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.

#### Nuclear Waste Vitrification

Due to its excellent high temperature properties, alloy 602CA has been used as "Vitrification Pots" by 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 Westinghouse Savannah River company<sup>(17)</sup> again confirmed the excellent behavior of alloy 602CA for use as top head and off gas components in the Defense Waste Processing Facility (glass-smelter) at the Department of Energy's Savannah River site.

## 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 the newly developed alloy 602CA as evidenced by the various applications described above.

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.

#### REFERENCES

- 1. U. Brill & D. C. Agarwal, "Alloy 602CA A New High Strength, High Temperature Alloy for Service Temperatures up to 1200°C", Corrosion/93, Paper # 226, NACE International, Houston, Tx 1993
- 2. Krupp VDM GmbH: Material Data Sheet Nicrofer 6025H / 6025HT Alloy 602CA, Material Data Sheet No. 4037, Latest Edition dated November 2001
- 3. D.C. Agarwal and U. Brill, Material Degradation Problems in High Temperature Environments : Alloys Alloying Effects Solutions, Industrial Heating, October 1994, pp. 55-60
- 4. H.J. Grabke, E.M. Müller Lorenz, J. Klöwer, D.C. Agarwal, "Metal Dusting of Nickel Based Alloys", Materials Performance, Vol. 37, No. 7, pp. 58-63 (1998)

- 5. D.C. Agarwal, U. Brill, M. Metzler, "Practical Experience with the New Alloy 602CA: Application in Heat Treat Industry", Corrosion/93, Paper # 235, NACE International, Houston, Tx 1993
- 6. U. Brill and D.C. Agarwal, "Alloy 602CA A New Alloy for the Furnace Industry", ASM Proceedings of the 2<sup>nd</sup> International Conference on Heat Resistant Materials, Gatlinburg, TN, USA, September 11-14, 1995
- 7. D.C. Agarwal et al., "Innovations in Alloy Metallurgy for Furnace Rolls and Other High Temperature Applications", ASM Proceedings of the 2<sup>nd</sup> International Conference on Heat Resistant Materials, Gatlinburg, TN, USA. September 11-14, 1995
- 8. D.C. Agarwal and H. Klein, "Applications of New High Temperature Nickel Alloys in Various Industries", Applications and Materials Performance, Nickel Cobalt 97, Vol. 4, The Metallurgical Society of the Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, 1997, pp. 115-129.
- 9. J. Klöwer et al., "Metal Dusting and Carburization Resistance of Nickel Base alloys", Corrosion/97, Paper # 139, NACE International, Houston, TX 1997.
- 10. Rolled Alloys Data Sheet on Alloy 602CA, Form #1602, Feb. 2001, Rolled Alloys, 125 West Sterns Road, Temperance, MI 48182-9546, USA
- 11. N. Birks, G.H. Meir, F. S. Pettit, "High Temperature Corrosion Resistance", Journal of Metals, December 1987, pp. 28-31
- 12. R.C.John, "Engineering Assessment of Oxidation of Engineering Alloys", Corrosion/96, paper # 171, NACE International, Houston, TX 1996
- 13. U.Brill and D.C.Agarwal, "Carburization behavior of nickel and iron base alloys in the temperature range of 550 to 1200°C", Corrosion/2002, paper # 373, NACE International, Houston, TX 2002
- 14. U.Brill, "Mathematical Description of Carburization Behavior of Various Commercial Heat-Resistant Alloys", Heat Resistant Materials, Conference Proceedings, ed. by K.Natesan and D.J.Tillac, ASM International, Materials Park, Ohio, 1991, pp. 203-210
- 15. D.C. Agarwal et al., "Recent results on metal dusting of nickel base alloys and some applications", Corrosion/2001, paper # 382, NACE International, Houston, TX 2001
- 16. U.Brill and M. Rockel,"VDM Report # 25: High Temperature Alloys from Krupp VDM for Industrial Engineering", Krupp VDM, P.O.Box 1820, 58778 Werdohl, Germany
- 17. K.J. Imrich and C.F.Jenkins, "Material Performance in a Radio Active Waste/Glass Melter System Environment" Corrosion/96, paper # 135, Nace International, Houston, TX, 1996

# METALLURGICAL OPTIMIZATION OF ALLOY 602CA NOMINAL CHEMISTRY COMPARISON TO OTHER HIGH TEMPERATURE ALLOYS

Alloy	Fe	Ni	Cr	<u>Si</u>	C	Others
309	Bal	13	25	0.5	0.15	-
310	Bal	20	25	0.5	0.08	-
253	Bal	11	21	1.7	-	N,Ce
DS	Bal	36	18	2.2	0.06	-
800/800H	Bal	31	20	0.4	0.08	Ti, Al 0.4
120	Bal	38	25	0.6	0.06	Nb 0.7
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
230	1.5	Bal	22	0.4	0.10	W 14, Mo 1.2
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, Mo 9
617	1.5	Bal	22	-	0.06	Co, Mo 9, Al 1.2

# EFFECTS OF HIGH TEMPERATURE EXPOSURE ON GRAIN GROWTH FOR VARIOUS ALLOYS EXPOSED AT 2050°F (1121°C)

P	Average ASTM Grain Size Number						
Exposure ( <u>Hours</u> )	<u>602CA</u>	<u>601</u>	<u>601GC</u>	<u>600</u>	<u>353MA</u>	<u>330</u>	<u>333</u>
None (as annealed)	7	5	5.5	8	6	7	4
184	7	1	3.5	0	2.5	3	2.5
510	6.5	0	3	00	2	2	2
990	6.5	00	2.5	00	1.5	1.5	1

# TABLE 3

## HIGH TEMPERATURE MECHANICAL PROPERTIES OF ALLOY 602CA

	Room Temp <u>.</u> 25°C(77°F)	600°C <u>(1112°F)</u>	800°C <u>(1471°F)</u>	1000°C <u>(1832°F)</u>	1100°C <u>(2012°F)</u>	1200°C <u>(2192°F)</u>
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 Creep Strength (KSI)

Temperature <u>°C ( °F)</u>	$\underline{R_m}/10^5 h$	<u>R<sub>m</sub>/10<sup>4</sup>h</u>	<u>R<sub>p</sub>1.0/10<sup>5</sup>h</u>	<u>R<sub>p</sub>1.0/10<sup>4</sup>h</u>
650°C (1202)	20.3	31.2	17.4	26.8
700°C (1292)	14.5	22.5	12.3	19.1
800°C (1471)	2.90	6.10	2.40	4.60
900°C (1652)	1.40	2.60	1.10	1.90
950°C (1743)	1.00	1.90	0.80	1.30
1000°C (1832)	0.70	1.30	0.50	0.84
1050°C (1922)	0.45	0.90	0.28	0.52
1100°C (2012)	0.30	0.64	0.15	0.32
1150°C (2102)	0.20	0.44	0.06	0.15
1200°C (2192)		0.43		0.14

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

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

Exposure Temperature And Condition	<u>1,000 Hrs.</u>	<u>4,000 Hrs.</u>	<u>8,000 Hrs.</u>
Annealed Condition	Typical Value	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

TABLE 5CYCLIC OXIDATION DATA -- 1,200 HRS -- 24 HRS CYCLES

	<u>Weight change in mg / m<sup>2</sup>h</u>				
<u>Alloy</u>	<u>750°C</u>	<u>850°C</u>	<u>1000°C</u>	<u>1100°C</u>	<u>_1200°C</u>
602CA	+0.4	+3	+12	+7	-310
Х	+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	-

# TABLE 6 WEIGHT GAIN AND INTERNAL PENETRATION OF VARIOUS ALLOYS AFTER 3,000 HOUR EXPOSURE IN AIR AT 2100°F (1148°C)

<u>Alloy</u>	<u>Weight Gain ( mg / cm<sup>2</sup> )</u>	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	1.41
214	9.3	2.8
HR120	206	46.3
800HT	294	54.4

# CYCLIC CARBURIZATION BEHAVIOR IN CH<sub>4</sub>/H<sub>2</sub> ENVIRONMENT (A<sub>C</sub> = 0.8) IN TEMPERATURE RANGE 750°C – 1000°C

Alloy	<u>750°C</u>	<u>850°C</u>	<u>1000°C</u>
310	2	130	305
800H	4	143	339
625	4	105	204
617	2	50	64
Х	2	93	204
601	2	69	152
602CA	0	44	58

# Weight change (mg/m<sup>2</sup>h)

## TABLE 8

# TOTAL EXPOSURE TIMES AND FINAL WASTAGE RATES AFTER EXPOSURE IN CARBURIZING CO-H\_2-H\_2O GAS AT 650°C

<u>Alloy</u>	Surface	Total Exposure Time	Final Metal Wastage
i.	<u>Condition</u>	<u>in hours</u>	<u>Rate in mg/cm<sup>2</sup>h</u>
800H	ground	95	0.21
HK-40	-	190	0.04
HP-40	-	190	0.038
DS	ground	1988	4.3 x 10 <sup>-3</sup>
600H	ground	5000	0.033
601	black	6697	7.3 x 10 <sup>-3</sup>
601	polished	1988	4.9 x 10 <sup>-3</sup>
601	ground	10000	5.8 x 10 <sup>-4</sup>
C-4	ground	10000	$1.1 \ge 10^{-3}$
214	ground	9665 <sup>1)</sup>	$1.2 \times 10^{-3}$
160	ground	9665 <sup>1)</sup>	$6.3 \times 10^{-4}$
45TM	black	10000	$1.0 \ge 10^{-5}$
602CA	black	10000	1.1 x 10 <sup>-5</sup>
$617^{2}$	ground	7000 <sup>1)</sup>	$3.7 \times 10^{-6}$
690	ground	10000	$2.0 \times 10^{-6}$

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

<sup>2)</sup> Alloy 617 showed evidence of metal dusting after 7,000 hrs.

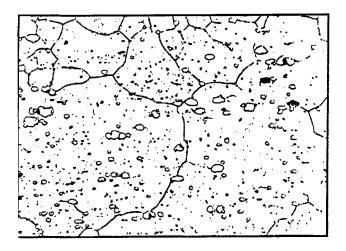


Figure 1 : Micrograph of alloy 602CA in the solution annealed condition 500x ( chromic acid etch)

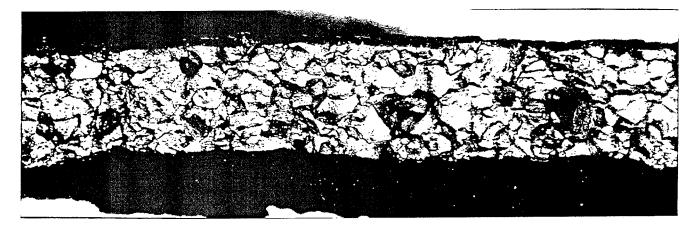
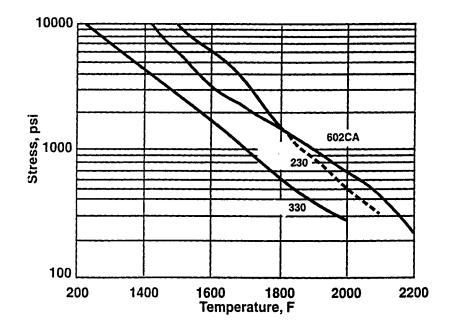


Figure 2A: Brittle fracture of an alloy 601 corrugated muffle from the combination of extensive grain growth and carburization



Figure 2B: Alloy 602CA grain growth after 3,150 hours exposure at 2100° F ( 1148° C ) ( Original grain size of ASTM 7 before exposure grew to ASTM 5.5 after exposure )



:Figure 3 : Average 10,000 hour Creep Rupture Strength for alloys 330, 230 and 602CA

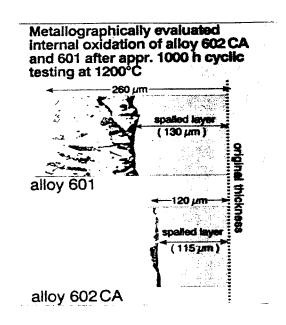
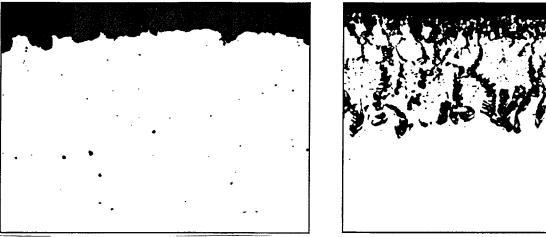


Figure 4: Internal Oxidation attack on alloy 601 in comparison to alloy 602CA after cyclic testing at 1200 °C in air for 1,000 hours



Alloy 602CA

Alloy 601

Figure 5 : Alloy 602CA and alloy 601 after 3,150 hours exposure at 2100°F ( 1148° C )

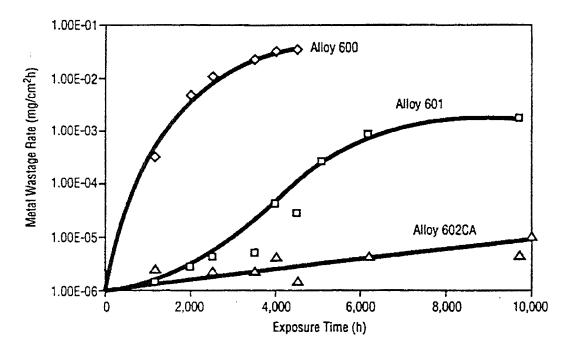


Figure 6: Metal wastage of nickel-base alloys 602CA, alloy 601, and alloy 600 due to metal dusting after exposure in strongly carburizing CO-H<sub>2</sub>O gas at 650°C

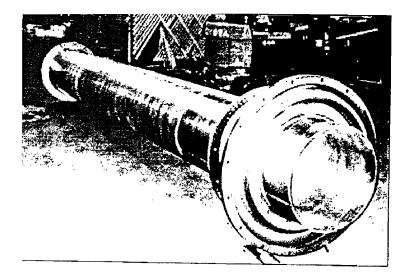


Figure 7: Alloy 602CA calciner for processing metal oxides (Alloy 602CA was selected over alloy 601 due to its greater scaling and creep strength)