UNCLASSIFIED

AD NUMBER
AD864932
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; 06 FEB 1970. Other requests shall be referred to Air Force Materials Laboratory, Wright-Patterson AFB, OH 45433.
AUTHORITY
AFML ltr dtd 12 Jan 1972

THIS PAGE IS UNCLASSIFIED

AD 864932

DMIC

review OF RECENT DEVELOPMENTS

DDC

Nickel-and Cobalt-Base Alloys

H. J. Wagner and W. F. Simmons

February 6, 1970

ALLOY DEVELOPMENT

Nickel-base Turbine-Vane Alloys

A new high-strength nickel-base alloy, possibly suitable for advanced turbine-stator-vane applications was recently developed by NASA/Lewis Research Center.(1) The alloy, designated WAZ-20, is nominally 17 to 20 tungsten, 6 to 7 aluminum, 1.4 to 1.6 zirconium, 0.10 to 0.20 carbon, and balance nickel.

Most advantageous at temperatures over 2000 F, WAZ-20 has a tensile strength of 20 ksi at 2200 F and over 40 ksi at 2000 F. When directionally solidified, its creep-rupture properties were better than in random polycrystalline material, and, in addition, its intermediate-temperature tensile strength and its ductility at temperatures from 1800 to 2175 F increased. The temperature at 15 ksi for a 100-hour creep-rupture life was 1945 F for the directionally solidified WAZ-20.

The impact toughness of WAZ-20 as cast and after aging for 1000 hours at 1600 F is considered to be excellent. Charpy V-notch values were 16-foot-pounds before aging and 20 foot-pounds after aging. Accordingly, these properties suggested that the alloy would resist foreign-object damage in engine applications.

Turbine-Blade Alloy for Thin Sections

A program has been started by TRW on the development of a turbine-blade casting alloy which can be used in thin sections without suffering the characteristic loss of ductility.(2) In recent years, the use of investment cast, air-cooled blades with very fine cooling passages has revealed a "section size effect"; that is, the thin sections are lower in ductility at intermediate temperatures and have poorer thermal-fatigue and creep-rupture properties than the bulk material. As a consequence, an effort has been initiated to develop an alloy which would have (1) as good tensile ductility in thin sections as in thick sections at intermediate temperatures, (2) a creep-rupture life of 100 hours at 1800 F/20 ksi, and (3) oxidation resistance at 1800 F equivalent to that of Udimet 700 at 1650 F.

An evaluation of Udimet 700, IN 100, IN 792, and TRW-NASA VI A alloys from these criteria resulted in the selection of the TRW alloy as a starting composition. The selection was based on the good rupture properties (which meet the program goals), the possibilities for improving ductility at the expense of creep-rupture strength and the possibilities for increasing corrosion resistance by coating. IN 792 had much better corrosion resistance, but since it met neither the ductility nor the creep-rupture goals, the conclusion was that the TRW-NASA VI A would have more potentiality for improvement to meet the goals.

Cobalt-Nickel γ'-Strengthened Alloy

A new high-temperature alloy was developed by NASA/Lewis Research Center by modifying their Co-25W-1Ti-0.5Zr-3.12Cr-0.6C alloy with nickel and aluminum to give gamma-prime strengthening.(3) The new alloy, designated NASA-SP, has the following composition in weight percent:

Co	37.4	Cr	2.11
Ni	38.0	Ti	1.01
W	14.0	Zr	0.25
Al	6.72	C	0.54

The alloy was developed by using the Box-Wilson experimental strategy for optimum seeking. While the scope was limited by optimizing only one condition of rupture life (1850 F/15 ksi) and by optimizing with respect to only four of the seven possible composition variables, the potential for using the Box-Wilson method in alloy development was believed shown.

The 100- and 1000-hour creep-rupture life of the as-cast NASA-SP was superior to that of commercial cobalt-base alloys (Figure 1) up to about 1825 F, but was inferior to that of nickel-base alloys over the entire range tested.

Despite its low chromium content, the alloy was equivalent to the currently used cobalt-base alloys in high-velocity cyclic oxidation tests, but had less resistance to oxidation than did the nickel-base alloys.

DISPERSION-STRENGTHENED ALLOYS

Cobalt Alloys for Turbine Vanes

Dispersion-strengthened cobalt alloys for turbine-vane applications are being studied by Pratt & Whitney.(4) Initial studies have centered on Co-20Ni-18Cr-$2ThO_2$ and Co-20Ni-30Cr-$2ThO_2$. Hot corrosion resistance was measured in a simulated turbine environment containing 0.2 ppm synthetic sea salt in the high-temperature portions of a cyclic

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MAAM).

W-P AFB, Ohio 45433

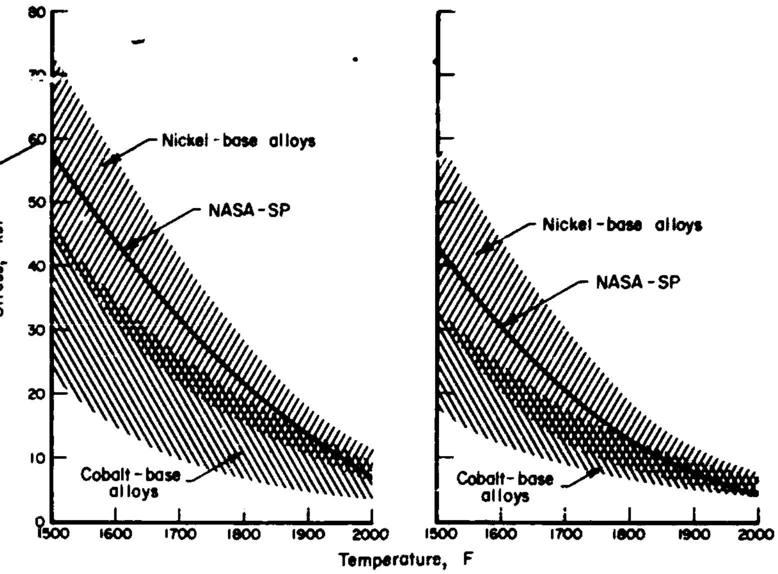

FIGURE 1. ISOCHRONAL STRESS-RUPTURE CURVES FOR ALLOY NASA-SP COMPARED WITH THOSE FOR COMMERCIAL CAST N EL- AND COBALT-BASE ALLOYS[3]

test. When coated, the Co-18Cr alloy successfully completed 1500 hours of test, while the Co-30Cr alloy failed at 900 hours because of propagation of internal defects nucleated during bar-stock fabrication. WI-52, tested for comparison purposes, had a useful life of only about 300 hours because of coating failure and subsequent rapid oxidation. Even when the Co-20Ni-18Cr-$2ThO_2$ alloy was not coated, oxidation weight gain was linear, and proceeded uniformly. Accordingly, this observation suggested that the alloy might be useful in some designs where a planned loss in component wall thickness could be tolerated.

Additional effort is under way to develop other coatings and brazing methods. Brazing trials indicate that both alloys may be brazed readily in vacuum with commercial nickel- and cobalt-base brazing alloys.

The microstructures of various dispersion-strengthened cobalt-base alloys have been examined by the Centre National de Recherches Metallurgiques so that a good basis for understanding the role of the matrix and dispersed phase in the strengthening mechanism could be obtained.[5] In addition to TD-Nickel, which was examined for comparison purposes, the following alloys were studied:

Co-0.2Zr-$2ThO_2$
Co-$4ThO_2$
Co-10Ni-0.2Zr-$2ThO_2$
Co-20Ni-18Cr-$4ThO_2$.

While sufficient data were not obtained to be able to correlate mechanical properties with particle content and morphology, matrix composition, or processing history, a good deal of information on the microstructure and matrix crystal structure and texture was presented.

Nickel-Base Alloys Dispersion-Strengthened By Comminution and Blending

An investigation was completed by NASA/Lewis to determine whether dispersion-strengthened nickel-base alloys could be made by comminution and blending, rather than by the chemical methods used in the commercially available materials.[6] Materials prepared by comminution, blending, sintering, and thermomechanical working showed tensile and creep-rupture properties at 2000 F that were equal to or better than those of comparable commercial ThO_2 dispersion-strengthened nickel. The best 2000 F tensile properties were obtained with a NiO-$4ThO_2$ composite ground in a heptane-alcohol mixture and selectively reduced to produce Ni-ThO_2. After 21 cold rolling and annealing cycles, the alloy had a tensile strength of 26 ksi at 2000 F. Creep-rupture strength at 2000 F was best in Ni-0.5Zr-$4ThO_2$ as well as in the Ni-$4ThO_2$.

As expected, the properties were found to be dependent on the thermomechanical processing, and small changes in powder processing and matrix composition influenced the response to thermomechanical processing.

DISLOCATION INTERACTION WITH GAMMA PRIME

The nature of the dislocation interaction with gamma prime in Waspaloy is being studied at the University of Michigan in order to cast light on the nature of edge-notch sensitivity of sheets of certain superalloys at 1000 to 1200 F under creep-rupture conditions.[7] Thus far, research on smooth sheet specimens has shown that in tensile tests at 1000 to 1400 F, the gamma-prime size strongly affects the dislocation mechanisms by which deformation occurs. Specifically, when the gamma prime is smaller than a critical size, the particles are sheared by the dislocations. On the other hand, above a certain critical size, the particles are bypassed by the dislocations (except possibly at high strains).

The mechanical properties were correlated with the nature of the interactions of the dislocations with the precipitate particles and the fracture mode. Thus, when the dislocations bypass the gamma-prime particle, the homogeneous deformation that occurs results in a higher elongation than that which results when localized deformation occurs as a result of gamma-prime shearing. The gamma-prime particle size might, therefore, be used as a basis for selecting aging treatments for optimum properties.

OXIDATION, CORROSION, AND PROTECTION

Cladding

Oxidation-resistant alloy claddings were investigated by the NASA/Lewis Research Center as a means of protecting superalloys against high-temperature oxidation.[8] As experimental materials, the nickel-base alloy IN 100 and the cobalt-base alloy WI-52 were used as substrates. The cladding, which was 5-mil sheet of Ni-30Cr-1.4Si, Ni-20Cr-4Al-1.2Si, and Fe-25Cr-4Al-1Y, was applied by gas-pressure bonding at 2000 F for 2 hours.

The clad substrates were exposed to cyclic furnace oxidation at 1900 and 2000 F for up to 200 hours. All three claddings provided good oxidation protection on both superalloys for 200 hours at 1900 F. At 2000 F, the Ni-Cr-Al-Si alloy protected IN 100 for 200 hours, and the Ni-Cr-Si and Fe-Cr-Al-Y alloys protected WI-52 for 200 hours. Figure 2 shows the results for 2000 F oxidation.

At least one element in the substrate had completely diffused through the cladding in 200 hours at 2000 F. Despite this, the protective ability of the best cladding/substrate combination mentioned above was not seriously degraded. In the other systems, however, the oxidation resistance had decreased significantly as a result of interdiffusion.

Diffusion Coating

The initial evaluation of various combinations of superalloys with diffusion coatings has been completed by TRW.[9] The overall objectives of the program are to develop coating systems for B1900, U-700, TD-Nickel-Chromium, MAR-M 246, TD-Cobalt, TRW VI A and MAR-M 509, such that the system could operate for 500 hours at 2200 F for turbine-vane alloys and at 1950 F for blade alloys. On the basis of static furnace oxidation tests and rig hot-corrosion testing, 15 coating/alloy systems were selected for more detailed investigation in Phase II.

Various modified diffusion coatings were examined. These included simple pack aluminide coatings, duplex aluminides (manganese-aluminum, cobalt-aluminum, chromium-aluminum, tantalum-aluminum, iron-aluminum, magnesium-aluminum), triplex aluminides (chromium-manganese-aluminum, cobalt-chromium-aluminum, iron-chromium-aluminum), codeposited aluminides (aluminum-chromium, aluminum-manganese, aluminum-magnesium, aluminum-yttrium), composite coatings containing inert oxides, slurry coatings, and pure nickel aluminide modifications.

The ratings of the various coating systems under hot-corrosion conditions are shown in Table 1.

Comparative Behavior

An investigation was conducted by NASA/Lewis Research Center to determine the resistance to oxidation and thermal-fatigue cracking of typical nickel- and cobalt-base gas-turbine alloys exposed alternately to high- and low-temperature, high-velocity gas streams.[10] The materials tested included nickel-base alloys IN 100, B1900, MAR-M 200, TAZ-8A, Hastelloy X, and TD-Nickel-Chromium and cobalt-base alloys L-605, X-40, MAR-M 509A, and WI-52. MAR-M 200 alloy was tested on conventionally cast (equiaxed structure), as directionally solidified, and as single-crystal castings. The controlled solidification castings were produced by a proprietary process. The test specimens were 4 x 1 x 1/4 inch with one of the long edges tapered to a 45-degree included angle to simulate the contour of an airfoil leading edge.

The cyclic test conditions were obtained through the use of a natural gas compressed-air burner which produced gas velocities up to mach 1 and specimen temperatures up to 2000 F. The standard test conditions required the specimen to be alternately heated for 1 hour at the specified test temperature and cooled for 3 minutes to room temperature. The cycling was normally continued for 100 hours, with the specimen being removed from the rig at 20-hour intervals for weighing, crack inspection, and surface-recession measurements. The

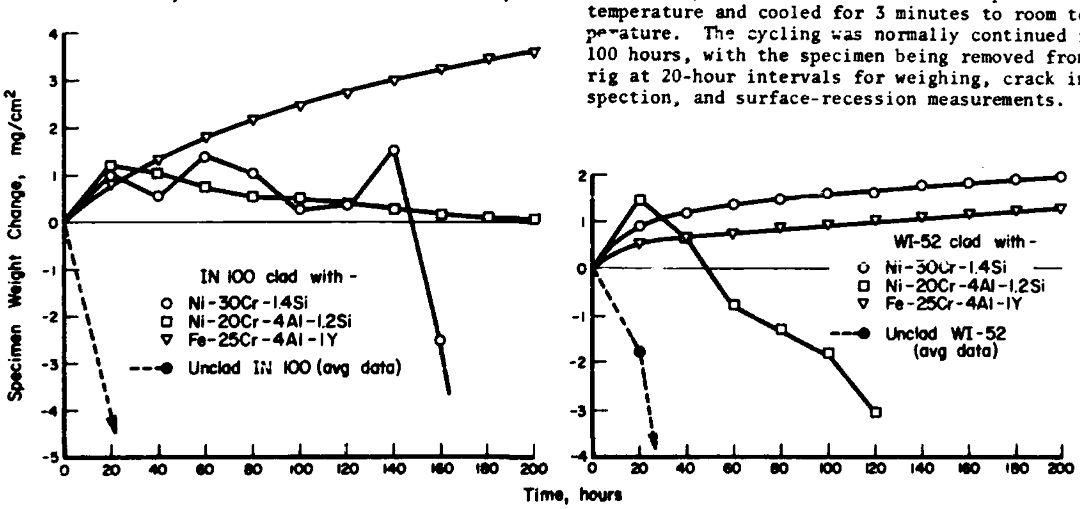

FIGURE 2. CYCLIC OXIDATION OF CLAD IN 100 AND WI-52 AT 2000 F[8]

(Specimens were cooled to room temperature after each 20-hour exposure.)

TABLE 1. RATINGS OF PHASE I COATING-ALLOY SYSTEM UNDER BLADE OR VANE CYCLE HOT-CORROSION CONDITIONS[9]

Alloy	Aluminides: Duplex Co	Mn	Cr	Ta	Fe	Mg	Triplex Cr-Mn	Co-Cr	Fe-Cr	Codeposited Y	Cr	Mn	Mg	Si
Blade Cycle														
B1900	oo	xx	xx	oo	xx	xx	xx	xx	xx	x	oo	xx	xx	--
TRW VI A	oo	xx	xx	oo	--	--	--	--	--	--	oo	xx	x	--
M-246	oo	xx	o	oo	--	--	--	--	--	--	oo	xx	xx	--
U-700	oo	x	o	--	--	o	oo	--	--	oo	oo	o	xx	--
Vane Cycle														
TD-NiCr	oo	o	xx	--	oo	oo	x	o	oo	oo	--	--	--	--
M-509	--	xx	x	--	oo	x	x	--	oo	oo	--	x	x	oo
TD-Co	--	xx	xx	--	--	xx	--	--	--	--	--	--	--	--
B1900	oo	x	x	oo	oo	x	oo	o	oo	oo	oo	oo	x	xx

Degree of Improvement Over Baseline Aluminide:

xx Significant (>50%)   x Some (<50%)
oo Detrimental   o None
-- Not tested

cooling-air-nozzle exit velocity was also mach 1. Three nonstandard test conditions were used for a limited number of tests: (1) standard conditions except mach 0.7 instead of mach 1 gas velocity during heating, (2) steady-state operation at mach 1 velocity with shutdowns every 10 hours (cooling was without forced air), and (3) operation at mach 1 but specimens cooled only to 1200 F before reheating.

The test results are summarized as follows:

(1) The weight-loss data for the standard tests are shown in Figure 3. Table 2 gives the weight-loss data for the nonstandard tests and a comparison with the standard tests. The nickel-base alloys as a class experienced less weight loss than did the cobalt-base alloys. The differences between materials were greater in mach 1 tests than in mach 0.7 tests.

(2) Under simulated steady-state operation (10-hour cycles with free air-cooling) at 2000 F, the average weight loss was less than that under standard conditions. Also, when the lower temperature was restricted to 1200 F, the weight loss decreased substantially for all alloys tested.

(3) After 100 hours at 2000 F using the standard cycle, the surface recession paralleled weight loss and ranged from 0.3 mil for B1900 and IN 100 to 50 mils for WI-52.

(4) Conventionally cast cobalt-base alloys were more resistant to thermal fatigue cracking than were conventionally cast nickel-base alloys. However, directionally solidified and single-grain castings of MAR-M 200 had no cracks even after 100 cycles at 2000 F. Also, the wrought nickel-base alloys Hastelloy X and TD-Nickel-Chromium were among the most crack-resistant alloys tested.

(5) Although the directionally solidified and single-grain castings of MAR-M 200 showed no thermal fatigue cracks, they had between two and five times as much weight loss as conventionally cast (equiaxed) castings (see Figure 4).

TABLE 2. EFFECT OF OPERATING CONDITIONS ON WEIGHT LOSS[10]
Maximum cycle temperature, T_{max}, 2000 F

Alloy	Weight Loss After 100 Hours at 2000 F, mg: Standard Cycle Mach 1(b)	Other Modes of Operatioi(a): Mach 0.7(b)	Mach 1(c)	Mach 1(d)
IN 100	250	395(1.58)	158(0.63)	169(0.68)
TD-NiCr	1,400	841(0.60)	1,091(0.78)	--
WI-52	23,700	22,116(0.93)	9,852(0.42)	9,840(0.41)
B1900	216	--	127(0.59)	145(0.67)
X-40	1,240	--	914(0.74)	--
MAR-M 509A	4,870	--	795(0.16)	--

(a) Values in parentheses are ratio of weight loss in other mode of operation to weight loss in standard cycle.
(b) Forced-air cool, T_{max} to room temperature, 1-hr cycles.
(c) Free-air cool, T_{max} to room temperature, ~10-hr cycles.
(d) Forced-air cool, T_{max} to 1200 F, 1-hr cycles.

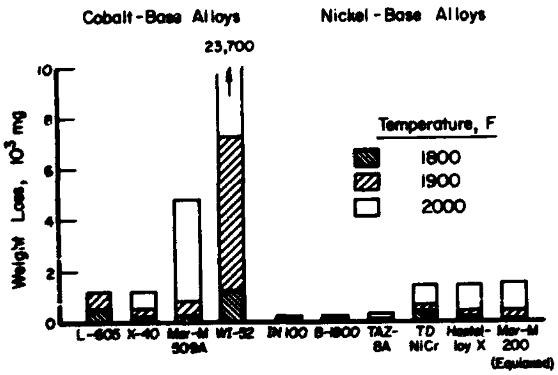

FIGURE 3. SUMMARY OF TOTAL WEIGHT-LOSS DATA FOR SPECIMENS EXPOSED 100 HOURS TO HIGH-GAS-VELOCITY OXIDATION APPARATUS[10]

(Specimens were 4 x 1 x 1/4 inches.)

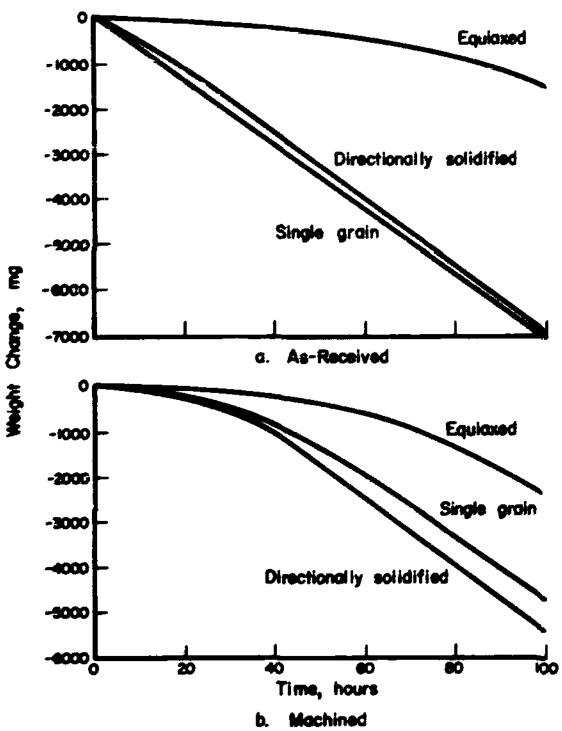

FIGURE 4. COMPARISON OF HIGH-GAS-VELOCITY OXIDATION BEHAVIOR OF THREE MACROSTRUCTURES OF MAR-M 200 AFTER EXPOSURE TO STANDARD CYCLE AT 2000 F MAXIMUM TEMPERATURE[10]

REFERENCES

(1) Waters, W. J., and Freche, J. C., "A Nickel Base Alloy, WAZ-20, With Improved Strength in the 2000 to 2200 F Range", Report NASA TN D-5352, NASA, Lewis Research Center, Cleveland, O. (August 1969).

(2) Preliminary information from TRW, Inc., Cleveland, O., on U.S. Air Force Contract F33615-69-C-1661.

(3) Sandrock, G. D., and Holmes, A. G., "Statistical Design and Analysis of Optimum Seeking Experiments to Develop a Gamma-Prime Strengthened Cobalt-Nickel Base Alloy", Report NASA TN D-5587, NASA, Lewis Research Center, Cleveland, O. (December 1969).

(4) Preliminary information from Pratt & Whitney Aircraft. United Aircraft Corporation, West Palm Beach, Fla., on U.S. Air Force Contract F33615-69-C-1668.

(5) Drapier, J. M., Coutsouradis, D., and Habraken, L., "Strengthening Mechanisms in TD-Cobalt Alloys", Final Report AFML-TR-69-145, Centre Nationale de Recherches Metallurgiques, Liege, Belgium, Contract F61052-67-C-0047 (September 1969).

(6) Quatinetz, M., and Weeton, J. W., "Dispersion-Strengthened Nickel Produced from Ultrafine Comminuted Powders", Report NASA TN D-5421, NASA, Lewis Research Center, Cleveland, O. (October 1969).

(7) Wilson, D. J., and Freeman, J. W., "The Dependence of Mechanical Characteristics of Waspaloy at 1000-1400 F on the Gamma Prime Phase", Report NASA CR-75572, University of Michigan, Ann Arbor, Mich., Contract NSL-23-005-005 (October 1, 1969).

(8) Gedwill, M. A., "An Evaluation of Three Oxidation-Resistant Alloy Claddings for IN 100 and WI-52 Superalloys", Report NASA TN D-5483, NASA, Lewis Research Center, Cleveland, O (October 1969).

(9) Preliminary information from TRW, Inc., Cleveland, O., on U.S. Air Force Contract F33615-68-C-1628.

(10) Johnston, J. R., and Ashbrook, R. L., "Oxidation and Thermal Fatigue Cracking of Nickel- and Cobalt-Base Alloys in a High Velocity Gas Stream", Report NASA TN D-5376, NASA, Lewis Research Center, Cleveland, O. (August 1969).

DMIC Reviews of Recent Developments present brief summaries of information which has become available to DMIC in the preceding period (usually 3 months) in each of several categories. DMIC does not intend that these reviews be made a part of the permanent technical literature. Copies of referenced reports are not available from DMIC; most can be obtained from the Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314.

R. W. Endebrock, Editor