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ALLOY DEVELOPMENT AND EVALUATION

Cast Nickel-Base Alloys

The purpose of a program completed at General Electric was to develop improved cast nickel-base superalloys through the additions of reactive metals to improve oxidation and hot-corrosion resistance. (1) The NASA-TRW VIA alloy was selected as the base alloy for the program and 27 alloys with additions of rhenium, manganese, yttrium, cerium, gadolinium, thorium, and lanthanum were studied. Static oxidation-resistance tests at 1800 F (1000 hours) and 2000 F (400 hours), and hot-corrosion tests at 1600 and 1750 F (up to 100 ppm NaCl) were used to evaluate the effect of the doping additions.

Lanthanum additions were effective in improvement of the short-time hot-corrosion resistance but in long-time tests, the results were negative. In addition, mechanical properties were seriously degraded. The doping additions apparently affect hot-corrosion behavior by their effects on surface oxide adherence rather than by an improvement in the hot-corrosion resistance of the overall alloy composition. It was concluded that the study concept is not adaptable to present investment casting practice.

Turbine-Blade Alloy for Thin Sections

The development program of a turbine-blade casting alloy with optimum properties in thin sections is continuing at TRW. (2) TRW-NASA VIA alloy was chosen as the baseline composition for a study of the effect of eight alloying elements (chromium, hafnium, tantalum, tungsten, aluminum, titanium, molybdenum, and vanadium). A computer analysis of screening-test data (1400 F tensile, 1800 F stress rupture, hot corrosion) indicated that chromium, tantalum, aluminum, tungsten, molybdenum, vanadium, and titanium all had significant effects on the target goals, while hafnium did not. Chromium and tantalum appeared to be beneficial or have no effect, while molybdenum, vanadium, and titanium appeared to be detrimental or have no effect. Aluminum and tungsten had a beneficial effect on life and strength, a detrimental effect on elongation, and no effect on hot corrosion.

The emphasis in formulating the compositions for Series III alloys, the next phase of the study, will be on ductility. In this regard, chromium will be studied at higher levels, and aluminum,

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tungsten, and molybdenum at lower levels. In addition, vanadium will be removed from Series III compositions, while hafnium, tantalum, and titanium will be kept at their present levels.

Evaluation of Alloys for Use in Hot Working

The high-temperature compressive yield strength and hot hardness of several heat-resistant alloys, including two cobalt- and three nickel-base alloys, were studied at Esco. (3) The alloys tested are identified in Table 1.

Each alloy was given the standard heat treatment with which it is commonly supplied, followed by exposure for 48 hours at the test temperature prior to testing.

The compressive yield tests were made on a Duffers Model 510 "Gleeble" testing machine, and the hot-hardness data were obtained using the mutual indentation method. The data are summarized in Figures 1 and 2.

TABLE 1. APPROXIMATE COMPOSITION, PERCENT

Alloy	C	Cr	Ni	Fe	Co	Other
35K	0.1	29	--	Bal	--	2Mn, 2Al
HH Type 2	0.3	24	13	Bal	--	--
HK	0.3	25	20	Bal	--	--
HN + Cb	0.3	25	27	Bal	--	1Cb
Incoloy 802	0.3	20	32	Bal	--	Al, Ti
Esco 58	0.5	23	31	Bal	2	2W, 2Zr, N
22-4-9 <sup>(a)</sup>	0.5	21	3.7	Bal	--	9Mn, N
49K	0.4	20	4.5	Bal	--	8Mn, N
49C	0.4	21	4.2	Bal	+	9Mn, N
49M	0.4	21	4.0	Bal	--	10Mn, Mo, N
Hastelloy X	0.1	20	Bal	21	1.4	9Mo, W
IN 100	0.15	10	Bal	--	14	4Al, 5Ti, 3Mo, Zr, B, V
MAR-M 200	0.15	9	Bal	--	10	11W, 4Al, 2Ti, 1Cb, Zr, B
Haynes 6B	1.0	30	2.5	--	Bal	Mo
Haynes 188	0.1	22	22	--	Bal	14W, La

(a) Wrought plate.

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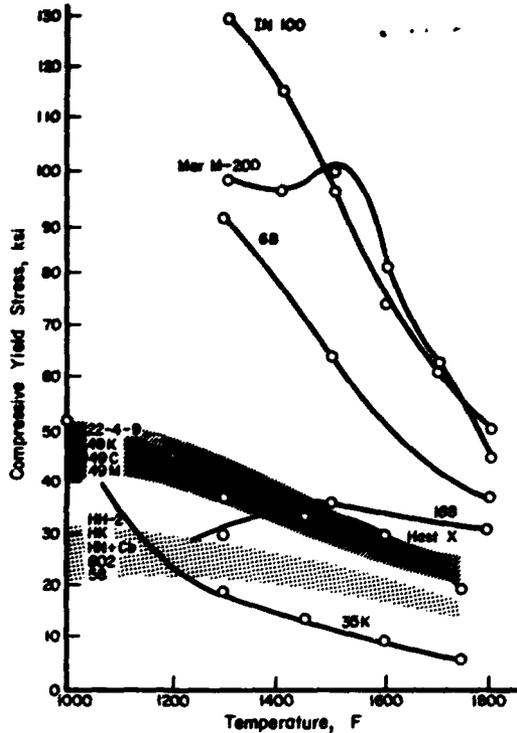


FIGURE 1. COMPRESSIVE YIELD STRENGTH<sup>(3)</sup>

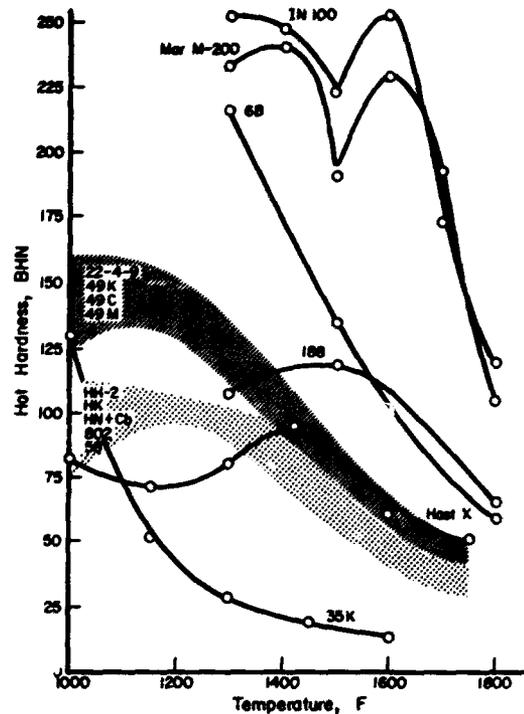


FIGURE 2. MUTUAL INDENTATION HOT HARDNESS<sup>(3)</sup>

In an excellent paper presented at the Steel Strengthening Mechanisms Symposium, in Zurich, Switzerland, R. F. Decker reviewed the mechanisms used to strengthen nickel-base superalloys.<sup>(4)</sup> Among the mechanisms and alloy-design techniques used to strengthen these superalloys are:

- (1) Solid-Solution Hardening of Gamma Phase: Many alloying elements strengthen the gamma solid solution. Aluminum, usually thought of only as a precipitation hardener, is a potent solid-solution hardener. Tungsten, molybdenum, and chromium also are strong hardeners, whereas iron, titanium, cobalt, and vanadium are weak hardeners.
- (2) Increasing the Volume Percent of Gamma Prime: This is a major technique of alloy designers. An increase from 14 to 60 percent gamma prime can quadruple the strength of superalloys.
- (3) Increasing the Stacking Fault Energy of Gamma Prime
- (4) Solid-Solution Hardening of Gamma Prime: At room temperature and 400 C (750 F), chromium, molybdenum, and tungsten strengthen gamma prime. At 800 C (1470 F), gamma-prime strengthening from titanium, columbium, and tantalum would be significant.
- (5) Increasing Coherency Strains for Temperatures Below 0.6 of the Melting Point

- (6) Decreasing Ripening (Increase in Size) Rate of Gamma Prime at Temperatures Greater Than 0.6 of the Melting Point
- (7) Minimizing the Formation of Eta, Ni<sub>3</sub>Cb, Laves, and Sigma Phases
- (8) Controlling Carbides to Prevent Denuded Zones, M<sub>23</sub>C<sub>6</sub> Grain-Boundary Films and Widmanstätten M<sub>6</sub>C
- (9) Stabilizing Grain Boundaries by Minute Additions of Boron, Zirconium, and Magnesium
- (10) Controlling Component Thickness/Grain-Size Ratio by Thermal Control and Heat Treatment
- (11) Controlling Crystal Orientation (Directional Solidification and Single Crystals)

DISPERSION-STRENGTHENED ALLOYS

Dispersion-Strengthened Cobalt Alloys for Turbine Vanes

Two thoria-containing cobalt alloys, Co-20Ni-18Cr-2ThO<sub>2</sub> and Co-20Ni-30Cr-2ThO<sub>2</sub>, were evaluated for turbine-vane applications in a program at Pratt & Whitney.<sup>(5)</sup>

Extrusion at 1900 F for the 18 percent chromium alloy and 2200 F for the 30 percent chromium alloy gave the best tensile and creep-rupture prop-

erties. The 18 percent chromium alloy has the better strength (both tensile and creep rupture) at test temperatures of 1800 and 2000 F, while the 30 percent chromium alloy was superior at 2200 F. The time-deformation curves for both alloys at 2000 F and 6000 psi and at 2200 F and 4000 psi are shown in Figure 3.

Oxidation erosion tests at 2000 and 2200 F and cyclic hot-corrosion tests at 2100 F indicate that both alloys compare favorably with presently used cobalt-base alloys, and the 30 percent chromium alloy is sufficiently resistant to be considered for uncoated vane service. The results of accelerated cyclic hot-corrosion tests at 2050 F using 35 ppm synthetic sea salt with heavy distillate fuels are given in Figure 4 in comparison with several conventional alloys and TD Nickel-Chromium.

OXIDATION, HOT CORROSION, AND PROTECTION

Turbine-Blade Alloys

The effect of very low levels of sulfur in JP-5 fuel on the hot corrosion of turbine-blade alloys is being evaluated at Phillips Petroleum.(6) Tests have been conducted in which 13 bare and 20 coating-superalloy systems were exposed at 15 atmospheres combustor pressure using air with 1 ppm sea salt and a fuel containing 0.040 weight percent sulfur and with exhaust-gas temperatures cycled from 1000 to 2000 F by control of fuel flow. Tests also will be made using fuel with 0.00040 percent sulfur and possibly at 0.0040 percent sulfur, depending on the results of the other tests.

To date, the tests indicate that the level of attack on most specimens is great enough to permit detection of differences in weight loss with the two levels of sulfur in the fuel if they exist.

Oxidation Behavior of Nickel-Base Alloys

Studies for the U.S. Air Force Materials Laboratory at the Central Institute for Industrial Research, Oslo, Norway, dealt with the oxidation behavior of several nickel-base alloys.(7) The program was carried out in four parts.

In Part I, the effect of different chromium/aluminum ratios on oxidation in air or oxygen at one atmosphere pressure was determined in the temperature range 800 to 1300 C (1470 to 2370 F). The nickel-base alloys studied contained chromium in the range of 3.8 to 14.4 and aluminum from 2.5 to 9.1 percent. The best oxidation resistance was obtained with the approximate composition Ni-9Cr-6Al. However, there was poor adherence of the oxide scale after cooling. The other three parts of the study were aimed at improving the adherence of the scale through minor additions of such metals as manganese, titanium, yttrium, and rare-earth metals.

In Part II, the effect of 2 percent titanium and 2 percent titanium plus 0.1 percent samarium additions on the oxidation of Ni-9Cr-5Al alloy was studied. The addition of titanium did not improve the oxidation characteristics of the base alloy at 900 C (1650 F). The addition of samarium improved the oxide adherence, but the mechanism was not determined.

In Part III, the effects of small manganese (0.2 to 1.2 percent) additions on the oxidation

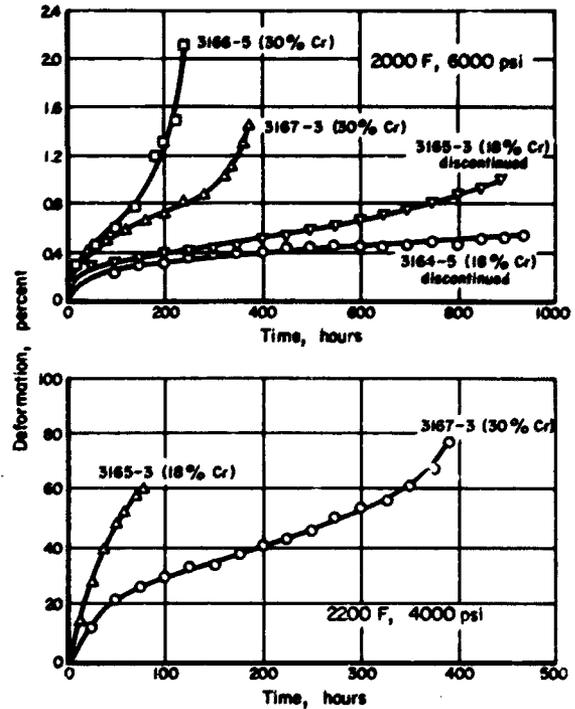


FIGURE 3. TIME-DEFORMATION CURVES FOR TD COBALT ALLOYS AT 2000 F AND 6000 PSI AND 2200 F AND 4000 PSI (5)

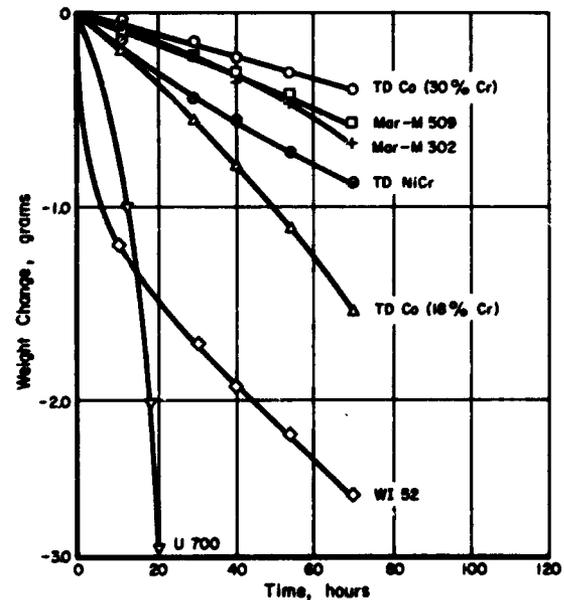


FIGURE 4. ACCELERATED CYCLE HOT-CORROSION TEST RESULTS FOR TD COBALT AND SELECTED ALLOYS (5)

behavior of two nickel-chromium and three nickel-chromium-aluminum alloys were studied. Although these studies have not been completed, little difference from the behavior observed for the nickel-chromium-aluminum alloys in Part I was noted. The Ni-8.5Cr-6Al base composition had the best oxidation resistance, but partial spalling of the oxide scale occurred on cooling.

In Part IV, the oxidation of three nickel-chromium-aluminum and two nickel-chromium-aluminum-columbium-manganese-silicon alloys with yttrium addition of 0.005 to 1.5 percent was studied. The effects of small yttrium additions, less than 0.1 percent, were difficult to evaluate, but larger additions had a marked effect on the microstructures, and improved oxide adherence. Yttrium appeared to enrich the grain boundaries, probably through the formation of a nickel-yttrium intermetallic compound. These alloys then showed a preferential oxidation of the grain boundaries which may have produced a mechanical keying effect to improve the scale adherence.

#### Effect of Pretreatments on Oxidation Behavior of NI-100

The effect of certain pretreatments on the oxidation behavior of nickel-base alloy IN-100 was recently studied at the Stanford Research Institute. (8) Internal oxidation occurred at 1000 C (1830 F) whereas oxidation at 1100 C (2010 F) resulted in a more protective continuous scale. This effect was attributed to the inert annealing treatments, since previous oxidation tests without pretreatments had resulted in extensive internal oxidation at both temperatures.

Electropolished specimens were preoxidized for 2 or 7 days at 800 C (1470 F), then annealed in an inert atmosphere either at 1000 or 1100 C (1830 or 2010 F). Subsequent oxidation testing was done at 1000 or 1100 C for times up to 200 hours. During prior investigations, the formation of NiO at 800 C in this alloy had been reported, but Al<sub>2</sub>O<sub>3</sub> and NiTiO<sub>3</sub> actually formed during the preoxidation treatments. Hence, the formation of a more protective oxide scale by a "displacement reaction" (Ni + Cr → Cr<sub>2</sub>O<sub>3</sub>) could not occur during inert annealing. Annealing at 1000 C did produce internal oxidation (Al<sub>2</sub>O<sub>3</sub>), but not at 1100 C. Extensive spalling of the oxide film during oxidation at both temperatures prevented the formation of a protective oxide scale on IN-100 alloy by this technique. Pretreatments at temperatures other than those employed (such as 1100 C) may prove beneficial.

#### Oxidation Study of WI-52 and IN-100 Alloys

An oxidation study of two superalloys, WI-52 and IN-100, in static air for 100 hours between 1500 and 2000 F was recently completed by NASA/Lewis. (9) The sequence of formation of the various oxides in these complex alloys was studied by high-temperature X-ray diffraction, *in situ*, during oxidation. Layering of the oxide phases was a problem in this study, but the results offered estimates of the relative amounts of each oxide in the scale.

In alloy WI-52, oxides were identified as CoO, CoCr<sub>2</sub>O<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Co<sub>4</sub>Co<sub>2</sub>O<sub>9</sub>. Although tungsten oxides were found, some tungsten was

thought to have dissolved in the columbium oxide. At 1600, 1800, and 2000 F, initially the scale was predominantly CoO, but CoCr<sub>2</sub>O<sub>4</sub> developed during longer exposure times. This change in the oxide structure occurred much faster as the temperature increased. Upon cooling to ambient temperatures, two important reactions were detected:

- (1) Subsurface -  $\text{CoO}_{1+x} + (1-3x)\text{CoO} + x\text{Co}_3\text{O}_4$  (spinel)
- (2) At surface -  $3\text{CoO} + 1/2\text{O}_2 + \text{Co}_3\text{O}_4$  (spinel)

A thin layer of Cr<sub>2</sub>O<sub>3</sub> was found at the metal/oxide interface, while CoCr<sub>2</sub>O<sub>4</sub> spinel (probably containing some CoWO<sub>4</sub>) was found in an intermediate layer. The outer layer consisted of CoO and a small amount of Co<sub>3</sub>O<sub>4</sub>.

The method of surface preparation had a greater influence on the nature of the oxides formed in these relatively short oxidation tests.

The oxidation of IN-100 alloy was more complex than WI-52 alloy as a function of both temperature and time. At 1500 and 1700 F, NiO was the predominant oxide, but TiO<sub>2</sub> also was of major importance in the early hours of testing at 1700 F. At 1900 F, early oxidation resulted in NiO and NiCr<sub>2</sub>O<sub>4</sub>, but NiTiO<sub>3</sub> and NiAl<sub>2</sub>O<sub>4</sub> oxides were formed with longer exposure times.

No phase changes were detected on cooling. NiO, TiO<sub>2</sub>, NiCr<sub>2</sub>O<sub>4</sub>, NiTiO<sub>3</sub>, NiAl<sub>2</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> were identified at one time or another, and the presence of ZrO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub> was suspected, as well.

#### Aluminide Coating on WI-52 Alloy

The oxidation resistance of cobalt-base superalloy WI-52 coated with a widely used commercial aluminide coating was evaluated by NASA/Lewis under cyclic conditions in furnace-air and in high-velocity combustion gas environments at temperatures from 1900 to 2100 F. (10) Cycle frequencies were varied from 1 to 100 hours in the furnace tests, while 1-hour cycles were used in the high-velocity tests. At all exposure temperatures, increased cycling accelerated coating degradation because the protective aluminum oxide scale spalled during cooling. Spalling depleted the coating of aluminum and permitted less protective oxides to form. In high-velocity tests, coating life decreased from 300 hours at 1900 F to 12 hours at 2100 F.

While the aluminide coated WI-52 alloy tested has good oxidation resistance at commercial-aircraft gas-turbine-engine conditions now in use, it does not appear to offer sufficient long-time protection under continuous high-temperature service at temperatures over 1900 F for use in advanced engines.

#### Future Needs

In a recent report, the Committee on Coatings of the National Materials Advisory Board pointed out some of the shortcomings of current coating systems and indicated some of the specific needs for gas-turbine applications as follows: (11)

- (1) For use in advanced engines, coatings must have a two-to-three-fold increase in useful life and a 200 F increase in maximum temperature capability to 2200 F.
- (2) The ability of manufacturers to coat small internal cooling passages is inadequate, and improved manufacturing techniques are needed.
- (3) Recoating of worn service parts results in excessive substrate attack, and improved recoating methods are required.
- (4) Current nondestructive-inspection techniques are not satisfactory, and improved methods are needed.

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