

depends on damage tolerance design to compensate for increased probability of structural degradation caused by fatigue or corrosion.

Summary

Damage tolerance design is a valuable asset at Lockheed-Georgia. The hard usage and harsh environments that the company's aircraft are subjected to in service has dictated adoption of damage tolerance concepts in all designs. In-service experience has proven the value of this approach in supplementing conventional design techniques.

Accordingly, the following steps relating to damage tolerance design are assiduously practiced at Lockheed-Georgia:

1) Every basic air and ground load supporting structure is designed to be tolerant of a reasonable amount of damage, regardless of its cause.

2) Achievement of desired damage tolerance levels is demonstrated analytically, and proven, where necessary, by structural tests.

3) Desired design fatigue life is analytically demonstrated with appropriate scatter factors. A factor of 4.0 is used where the analysis is supported by subcomponent tests. Where full-scale components, such as fuselages, wings, and the like, are subjected to fatigue tests, a factor of 2.0 is used in analysis.

4) The completed structure is subjected to complete airframe repeated load tests.

5) Finally, comprehensive maintenance inspection methods, periods, and procedures are established and recommended to the user.

By combining damage tolerance design with conventional fatigue resistance and repeated load techniques, aircraft designed and produced by Lockheed-Georgia have greatly enhanced reliability, maintainability, and operational safety characteristics.

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SEPT.-OCT. 1969

J. AIRCRAFT

VOL. 6, NO. 5

NASA Programs for Development of High-Temperature Alloys for Advanced Engines

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An intensive research effort is underway at the NASA Lewis Research Center to provide improved materials for the hot components of advanced aircraft gas turbine engines. Research is being conducted both in-house and under NASA sponsorship to develop advanced materials for such applications as stator vanes, turbine buckets and disks, combustion chamber liners, and the latter compressor stages. Major areas of work deal with the development of nickel and cobalt base alloys, chromium base alloys, dispersion strengthened materials, composite materials, and protective coatings. Progress in NASA programs dealing with all these areas is described.

Introduction

TO increase performance, advanced aircraft gas turbine engines must use higher turbine inlet gas temperatures. Air cooling permits materials to be used at elevated gas temperatures. However, cooling must be paid for by increased engine complexity and by some sacrifice in performance, when compared with the same temperatures, if achieved without cooling. It therefore remains an important objective to provide materials that will survive at higher temperatures thus permitting higher gas temperatures—either without cooling or at least with reduced cooling requirements. There is a need for improved high-temperature materials for engine compo-

nents such as stator vanes, turbine buckets and disks, transition ducts, combustion chamber liners, and the latter compressor stages. The NASA Lewis Research Center is actively participating in research to provide advanced materials for such applications both by conducting in-house work and by funding research in other organizations.

Depending upon the engine component, materials must operate at temperatures ranging between approximately 1200 and 2200°F (649 and 1204°C). For such applications as the SST, the operating time requirement is on the order of thousands of hours. Superimposed upon the temperature and time requirements are other factors such as stress, strain, thermal and mechanical fatigue, and the erosive, corrosive effects of high-velocity combustion gases.

Cast and wrought nickel base alloys and to a lesser extent cobalt base alloys have been and continue to be the workhorse materials for the hot components of gas turbine engines. Current nickel base alloys contain a large number of alloying constituents that contribute to one or more of three basic

Presented at the Sixth Congress of the International Council of the Aeronautical Sciences, Munich, West Germany, September 9-13, 1968; submitted October 15, 1968; revision received May 5, 1969.

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Table 1 Nominal compositions of nickel and cobalt-base alloys

Alloy	Weight %														
	C	Mn	Si	Cr	Ni	Co	Mo	W	Nb	Fe	Ti	Al	B	Zr	Others
NASA TAZ-8	0.125	6	Bal	...	4	4	6	...	1	8Ta, 2.5V
NASA TAZ-8A	0.125	6	Bal	...	4	4	2.5	6	0.004	1	8Ta
NASA TAZ-8B	0.125	6	Bal	5	4	4	1.5	6	0.005	1	8Ta
NASA-TRW VIA	0.13	6.1	Bal	7.5	2	5.8	0.5	...	1	5.4	0.02	0.13	0.5Re, 9Ta, 0.43Hf
IN-100	0.18	10	Bal	15	3	4.7	5.5	0.014	0.06	1V
INCO-713C	0.12	12.5	Bal	...	4.2	...	2	...	0.8	6.1	0.012	0.10	...
B-1900	0.10	8	Bal	10	6	1	6	0.015	0.10	4Ta
MAR-M200	0.15	9	Bal	10	...	12.5	1	...	2	5	0.015	0.05	...
RENE' 41	0.09	19	Bal	11	10	3.1	1.5	0.005
NASA Co-W-Cr	0.4	3	...	Bal	...	25	1	0.5	...
NASA Co-W-Cr-Re	0.4	3	...	Bal	...	25	1	0.5	2Re
X-40	0.5	0.75	0.75	25.5	10.5	Bal	...	7.5
WI-52	0.45	0.25	0.25	21	...	Bal	...	11	2	2
MAR-M302	0.85	21.5	...	Bal	...	10	0.005	0.2	9Ta
L-605	0.05	2 max	1 max	20	10	Bal	...	15	...	3 max
	to 0.15														

alloy strengthening mechanisms, intermetallic, solid solution, and carbide strengthening. The most important single factor contributing to the retention of high-temperature strength in nickel base alloys is precipitation of the Ni_3Al intermetallic phase, known as gamma prime. This phase has the useful facility of being able to take into solution various quantities of other elements without changing its basic crystal structure face-centered cubic (fcc). The presence of these elements in gamma prime can significantly alter the properties of the phase and therefore the alloys. Cobalt base alloys, due to the lack of a potent strengthening mechanism such as the gamma prime phase, have lower strength than nickel base alloys over most of their useful temperature range. However, above approximately 2050°F (1121°C), the maximum solutioning temperature of gamma prime, cobalt base alloys tend to have higher strength when oxidation can be controlled. The higher melting point of cobalt (2720°F, 1493°C) compared to that of nickel (2650°F, 1454°C) also suggests that cobalt base alloys may have useful strength to higher-temperature levels.

Dispersion strengthened materials offer considerable promise for extending the useful temperature range of base metals. A notable example is TD nickel and its modifications in which a fine, extremely stable dispersion of ThO_2 particles is provided in a nickel or nickel-chromium matrix. These materials have great promise as wrought alloys for use in stator vanes up to approximately 2400°F (1316°C). However, the strength of the dispersion strengthened materials currently available is not adequate for turbine blade applications.

Composite materials also afford great potential for vastly increasing high-temperature strength capability. Fibers of high melting point materials such as tungsten can be enclosed in a lower melting point metal or alloy matrix to achieve outstanding high-temperature strength. The development of this category of materials is still in its infancy, but if problems of incompatibility between the fibers and matrix can be overcome substantial gains may be realized.

Chromium alloys represent another major class of materials with potential for application to the hot sections of aircraft turbine engines. Because of its high melting point (3434°F, 1890°C), chromium should retain useful strength to higher temperatures than either nickel or cobalt base alloys. However, problems associated with inherent low-temperature brittleness and severe nitrogen embrittlement resulting from high-temperature exposure to air must be overcome before the high-temperature strength advantage of chromium alloys can be utilized in turbine engines. For use at even higher temperatures, alloys of the refractory metals tantalum and ni-

bium deserve consideration. However, their inherently poor oxidation resistance is a serious deterrent to their use.

Associated with all of these materials is the need to provide satisfactory protective coatings to resist the erosive-corrosive action of high-velocity combustion gases in the hot sections of the turbine engine. The need for such coatings varies in degree depending upon the base metal being considered. Thus, chromium alloys probably are unlikely to be used in an air environment until satisfactory coatings are developed. This would also hold true to an even greater degree for the very refractory metals such as columbium and tantalum. However, even nickel and cobalt base alloys require coatings if they are to be used economically and up to their highest use temperature potential.

All of the preceding developmental areas are under investigation either at the NASA or under NASA sponsorship. Some of the highlights of this research are described in the ensuing sections of this paper.

Nickel and Cobalt Alloy Research

Since the development of Nimonic 75 in the 1930's, the high-temperature strength of nickel base superalloys has gradually improved. Similarly, cobalt base alloys have been improved in high-temperature strength starting with X-40 which was used in World War II turbine engines. Significant improvements have also been made in oxidation resistance and ductility.

Conventionally Cast Alloys

Table 1 lists the nominal compositions of several NASA nickel and cobalt base alloys as well as representative commercial alloys. The TAZ-8 nickel base alloy series and the cobalt-tungsten alloy series resulted from in-house research programs.¹⁻¹⁰ The NASA-TRW VI-A nickel alloy was developed at TRW Inc. under NASA sponsorship.¹¹

High-temperature strength

Figure 1 compares the stress-rupture properties of alloys VI-A and TAZ-8 with currently used cast nickel base alloys at 15,000 psi. All of the alloys shown are in the random polycrystalline form. Alloy VI-A shows approximately a 50°F improvement in use-temperature over its nearest competitors and has a 1000-hr life at 1875°F and 15,000 psi. The TAZ-8 alloys, although basically cast materials, have also been successfully fabricated into bar and sheet. For example,

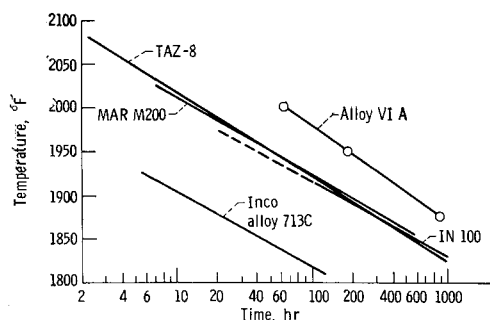


Fig. 1 15,000 psi stress-rupture properties of cast nickel base alloys.

thickness reductions of 50% were obtained with $\frac{1}{2}$ -in. diam as-cast bars by unidirectional forging techniques at room temperature.⁴ Cast slabs of TAZ-8A, 0.110 in. thick were rolled into sheet strips approximately 0.020 in. thick.⁷ Such workability potential is beneficial in that it broadens the applicability of these alloys and they need not be limited solely to cast configurations.

Figure 2 illustrates the as-cast, stress-rupture properties of two NASA cobalt base alloys. These alloys, due to their low chromium content, are significantly different in composition from currently used cobalt base alloys which all contain chromium in quantities between 21 and 28%. Despite their low chromium content catastrophic oxidation clearly did not occur with either of these alloys in the unprotected condition, even at the highest test temperatures. This is reflected by their good high-temperature stress-rupture performance. However, it must be recognized that adequate protective coatings must be developed for these alloys if they are to be used for long-time turbine applications. These alloys, although basically cast materials, are also readily workable.^{9,10} Although originally designed for space power system applications their excellent high-temperature strength suggests potential use for stator vane applications in advanced turbine engines. Further developmental work with this alloy series toward this end is under way at NASA.

Oxidation resistance

Other properties besides strength must be considered in designing alloys for gas turbine engine applications. One of the most important of these is oxidation resistance. Figure 3 compares the static oxidation behavior of various nickel base alloys at 1900°F (1038°C) on a conventional weight gain basis. In the vacuum-melted condition TAZ-8A compares favorably with all of the other alloys up to 310 hr, but the steeper slope of its weight gain curve suggests that its oxidation resistance would be less than that of MAR-M200 after longer exposure times. Oxidation data were not obtained at the same test conditions with either TAZ-8B or alloy VI-A so that a direct comparison cannot be made on this plot. However, their

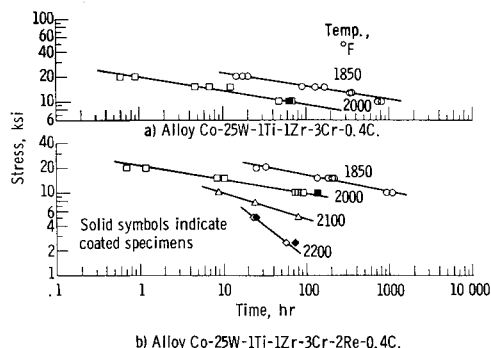


Fig. 2 Stress-rupture properties of chromium and chromium-rhenium modified cobalt base alloys.

oxidation resistance as determined from other tests and visual examination of tested stress-rupture specimens is about equivalent to that of TAZ-8A. It must be emphasized however, that conventional static oxidation tests do not constitute a final evaluation of an alloy's oxidation resistance in the complex gas turbine environment.

Static oxidation data are useful as a yardstick for screening purposes. To fully evaluate an alloy for oxidation-erosion resistance, dynamic tests must be conducted in which the alloys can be exposed to alternate cycles of high and low temperatures in gas streams having velocities up to Mach 1. Such current studies are discussed in a later section of the paper.

Microstructural stability

Exposure for several thousands of hours at temperature can alter the phases present in nickel and cobalt base alloys as well as their morphology. Formation of a sigma phase has been observed in nickel base alloys after long-time service exposure in the 1450 to 1700°F (788 to 927°C) temperature range.¹² Formation of this phase can significantly reduce tensile ductility as well as creep-rupture life. It is possible to predict with reasonable accuracy whether or not an alloy will form sigma by calculating the electron-vacancy concentration \bar{N}_V of the residual matrix after other phases such as gamma prime and the carbides have precipitated.¹³ If the calculated \bar{N}_V is below the cutoff point for stability as determined from experimental data for representative nickel base alloys, sigma phase would not be expected to form. The \bar{N}_V for TAZ-8A and TAZ-8B were 2.26 and 2.27, respectively,⁸ well below the safe upper limit of 2.59. The \bar{N}_V for alloy VI-A was 2.17. Exposure of both TAZ-8B and the VI-A alloy for 1000 and 1500 hr, respectively, at 1600°F (871°C) did not result in sigma phase formation in either alloy.

Other embrittling phases besides sigma can form in superalloys. A notable example is the Laves phase observed in the widely used cobalt base superalloy L-605. By reducing silicon,¹⁴ which stabilizes the Co₂W Laves phase in this alloy, the amount of Laves phase precipitation could be lessened and postaging ductility increased. This is shown in Fig. 4. Introduction of cold work prior to aging, to change the nature of the precipitation from a preferential intergranular type to a more homogeneous type within the grains, also improved the postaging ductility of this alloy.¹⁵ The importance of maintaining good ductility in turbine engine materials cannot be overstated since both thermal and mechanical fatigue resistance can be adversely affected if it is lowered.

Directionally Solidified Alloys

At high temperatures, a frequent failure mode in cast nickel base alloys is intercrystalline fracture along grain boundaries

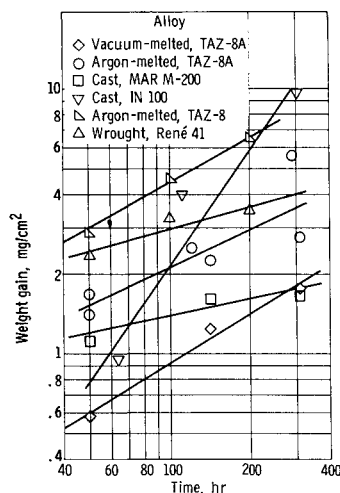


Fig. 3 Oxidation behavior of several nickel base alloys at 1900°F.

transverse to the major stress axis. Ver Snyder and Guard have shown that improved strength and ductility can be obtained if such boundaries are eliminated.¹⁶ Also, Pearcey and Ver Snyder showed that improvements in high-temperature strength and intermediate-temperature ductility could be obtained with MAR-M200 (PWA 659) by directional solidification.¹⁷ Directional solidification techniques were applied to TAZ-8B to produce test specimens with a columnar grain orientation. Figure 5 compares the tensile properties of random and directional polycrystalline TAZ-8B. Improvements in both intermediate-temperature strength and ductility over the entire temperature range considered were obtained by directional solidification. It should be noted that a columnar grain structure is particularly desirable in turbine buckets that are primarily under centrifugal stress, and that controlled solidification can be a powerful tool in extending the high-temperature capability of superalloys for turbine applications.

Coatings for Nickel and Cobalt Base Alloys

In current aircraft gas turbine engines, maximum operating temperatures of nickel and cobalt base alloys are determined primarily by strength considerations. Even in these engines, however, protective coatings are commonly used to extend the time between overhauls since they reduce the detrimental effects of oxidation and erosion by particles in the hot gas stream.

In the U. S., most coatings for nickel and cobalt base superalloys have been developed by commercial coatings vendors or engine manufacturers who have kept much of their data proprietary. Therefore, there is very little quantitative information available regarding the time and temperature capabilities of coated nickel or cobalt base alloys and the factors that limit their life in high-temperature service. Since such information is essential to an orderly program for improvement of coatings, NASA has sponsored work at the Solar Division of the International Harvester Company to evaluate selected commercial protective coatings applied to cobalt and nickel base alloys. Performance of these materials is being determined in erosion-oxidation rigs wherein the materials are subjected for long times to high-velocity (Mach 0.86) combustion gases at temperatures in the range of 1700 to 2200°F (927 to 1204°C). Such rig testing is designed to simulate as closely as possible in a relatively inexpensive, controlled laboratory test major environmental factors involved in aircraft engine application such as high-velocity gas flow, repeated thermal cycling, and thermal shock.

For this study, commercially available coatings were applied by coatings vendors onto airfoil shaped specimens of two nickel alloys, IN-100 and B1900, and two cobalt alloys, X-40 and WI-52. (Detailed information on substrate composition, surface finish, shape, etc. are reported in Ref. 18.) Three coatings were evaluated on each of these substrates; these are believed to be representative of the best superalloy coatings currently available in the U. S.

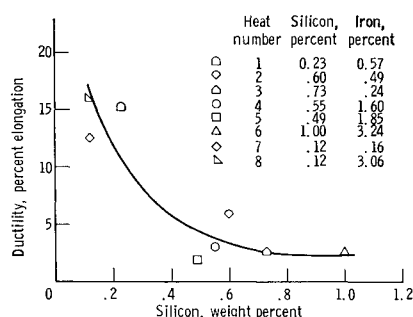


Fig. 4 Effect of silicon on room temperature ductility of L-605 sheet after 1000 hr at 1600°F.

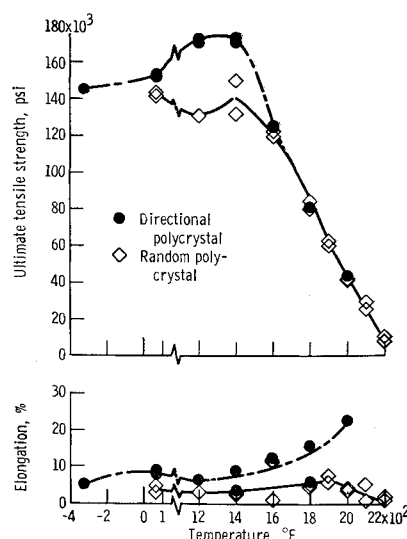


Fig. 5 Tensile properties of TAZ-8B.

Before testing, the coatings were carefully characterized. Metallographic examination was used to determine coating thickness, uniformity of coverage, distribution of phases, and the hardness variation across the coating and substrate. Electron microprobe analyses were used to establish the distribution of major elements in the coating and substrate. In addition, phases present on the surface of the specimen were identified by standard x-ray diffraction techniques. Some of the results of this pretest characterization of the coatings are summarized in Table 2.

It is evident that all of the coatings are of the aluminide type, formed in most cases by reaction between aluminum and the major substrate elements. However, there appear to be significant compositional differences between the coatings applied by the various vendors, and in some cases, it is evident that elements such as chromium, iron, titanium, and silicon were deposited along with aluminum in the coating process. It is anticipated that similar characterization and analyses after long-time exposure in the burner rigs will identify those factors responsible for degradation and failure of the coatings.

From the limited data available at this time, it appears that the best coatings on nickel base alloys have lives in the burner rig tests under cyclic conditions of several thousand hours at maximum temperatures in the range 1800 to 1900°F (982 to 1038°C). Coated cobalt base alloys are significantly less oxidation resistant than coated nickel base alloys. For advanced engines, improved coatings will be needed for both classes of alloys.

Dispersion Strengthening

Ever since the production of dispersion-strengthened aluminum by Irmann in 1946,¹⁹ investigators have attempted to achieve similar gains in strength in higher melting point metals. Some of the most promising results have been obtained with the nickel-thoria system using a colloidal-chemical approach.²⁰ Materials of this type have creep-rupture properties that should permit increased material temperatures for stator vanes and other low-stress applications, but they do not have high enough strength for turbine bucket applications.²¹ One route to achieving higher-strength systems is to combine solid solution and precipitate strengthening with the dispersion (and thermomechanical) strengthening. NASA is actively participating (along with others) in this effort.

An initial objective in development of dispersion-strengthened materials is to determine whether a particular process is capable of producing the desired distribution in terms of particle size and interparticle spacing of stable particles (e.g., oxides) in the particular metal matrix of interest. The

Table 2 Summary of distinguishing coating parameters (Ref. 18)

Alloy and coating	Coating thickness, ^a mils	Coating phases	Electron microprobe analysis, atomic % ^b	Remarks
IN-100				
B	2.5	Outer layer— MAl_3 Matrix phase— MAl Interface phase— M_3Al	15Ni, 3Cr, 3Ti, 2Co, 77Al (S) 23Ni, 2Cr, 23Ti, 4Co, 49Al (T) 41Ni, 12Cr, 9Ti, 11Co, 27Al (S)	Ti added; no interface voids; aluminum rich outer layer
C	2.6	Matrix phase— MAl Interface phase— M_3Al	48Ni, 3Cr, 6Co, 43Al (T) 53Ni, 11Cr, 11Co, 25Al (T)	Cr and Si added; no interface voids
D	5.5	Outer layer— Cr_3Al_2 Matrix phase— MAl Interface phase— M_3Al	41Cr, 7Fe, 1Co, 51Al (T) 8Cr, 30Ni, 3Fe, 9Co, 50Al (T) 16Cr, 43Ni, 5Fe, 11Co, 25Al (T)	Cr and up to 20 wt % Fe added; some coating spall; no voids; aluminum chromide outer layer
B 1900				
F	2.9	Outer layer— M_2Al_3 Matrix phase— MAl Interface phase— M_3Al	24Ni, 4Cr, 2Co, 70Al (T) 44Ni, 4Cr, 4Co, 48Al (T) 38Ni, 9Cr, 7Co, 18Mo, 28Al (T)	Si added, very uniform coating; no interface voids; aluminum rich outer layer
G	2.3	Outer layer— MAl Dispersed phase— Cr_2Al Interface phase— M_3Al	43Ni, 2Cr, 6Co, 1Fe, 48Al (T) 3Ni, 55Cr, 2Co, 2Mo, 38Al (S) 50Ni, 22Cr, 8Co, 20Al (T)	Cr and up to 2 wt % Fe added; some coating spall; severe interface voids
H	3.0	Matrix phase— MAl Dispersed phase— M_3Al Interface phase— M_3Al	42Ni, 4Cr, 3Co, 51Al (T) 46Ni, 16Cr, 1Co, 37Al (S) 38Ni, 21Cr, 7Co, 4Ti, 30Al (S)	Possible Ti and Cr addition; no interface voids
X-40				
J	1.6	Matrix phase— MAl Dispersed phase— Cr_2Al	4Ni, 22Cr, 30Co, 44Al (T) 2Ni, 47Cr, 15Co, 36Al (S)	Possible Cr addition; no interface voids
K	1.6	Matrix phase— MAl Dispersed phase— Cr_2Al^c	7Ni, 13Cr, 29Co, 51Al (T)	Coating spall; thickness variation; interface voids
L	1.3	Matrix phase— MAl Dispersed phase— MAl Interface phase— MAl	9Ni, 7Cr, 32Co, 2Ti, 50Al (T) 6Ni, 7Cr, 38Co, 4Ti, 45Al (S) 5Ni, 19Cr, 26Co, 50Al (S)	Ti added; no interface voids
WI-52				
N	1.7	Matrix phase— MAl Dispersed phase— Cr_2Al^c	46Co, 9Cr, 45Al (T)	Possible Cr and Si additions; some interface voids
O	1.2	Matrix phase— MAl Dispersed phase— Cr_2Al^c	42Co, 6Cr, 52Al (T)	Possible Cr addition; some interface voids
P	2.2	Matrix phase— MAl Dispersed phase— Cr_2Al^c	42Co, 3Cr, 55Al (T)	Possible Cr addition; some interface voids

^a Average thickness of both sides of specimen.^b T = transverse electron microprobe analysis; S = spot electron microprobe analysis.^c Based on electron microprobe analysis and x-ray data correlations for the J coating.

goal is to maintain an average particle size of less than 0.1μ and an interparticle spacing less than 2μ .

The primary approach being studied at the Lewis Research Center is the "comminution and blend" method which involves the blending of ultrafine powders of the metal matrix and the oxide dispersoid to achieve the desired dispersion. Ultrafine oxide particles are available. To achieve the desired interparticle spacing, metal powders appreciably smaller than the desired interparticle spacing are required.²² Methods of comminution for metals and alloys have been developed²³ that permit the production of ultrafine ($<0.5 \mu$) metal powders. Recent work with the comminution and blend method²⁴ resulted in Ni + Al_2O_3 materials with particle sizes of 0.04μ (median size) and an interparticle spacing of 1.84μ . The range of sizes was 0.017 to 0.31μ . This work has also shown the importance and the ability to maintain careful control of cleaning and densification rates so as to prevent small quantities of impurities from causing detrimental reactions either in subsequent processing or use. Mechanical milling and blending methods offer a number of advantages, including relative ease of applicability and low cost of production, as well as flexibility of the method as regards its applicability to complex alloys. Thus, mechanical milling may be applied as readily to a highly alloyed matrix as to a simple metal base. Colloidal chemical methods, on the other hand, are quite difficult to apply rapidly to a wide variety of alloy compositions. Dispersion strengthening affords great promise for extending the use temperature capability of nickel and cobalt base alloys.

Composite Materials

Another approach to improving the strength and temperature capabilities of nickel and cobalt base materials is to

develop composite materials in which an inherently oxidation resistant superalloy matrix is strengthened with more refractory high-strength fibers. A program is being conducted at NASA's Lewis Research Center to develop such composites in which small diameter refractory metal or alloy fibers are embedded in a nickel alloy matrix.²⁵

The major problem encountered in developing such composites has been degradation of the strength of the refractory alloy fibers as a result of interdiffusion with nickel and/or other constituents of the alloy matrix. Progress has been made in minimizing the extent of such interactions. The creep-rupture strength of composites can be optimized by proper fiber diameter selection. Generally, small-diameter fibers are more advantageous than large-diameter fibers for short-time creep-rupture applications. For long-time applications, the opposite is true in systems where strength is degraded by interdiffusion.

Composites of refractory metal-fiber reinforced nickel base alloys have been produced which have stress-rupture properties superior to conventional superalloys at use temperatures of 2000 and 2200°F (1093 and 1204°C). For example, a composite consisting of 70 vol. % of 0.015 -in.-diam tungsten wires embedded in a Ni-25W-15Cr-2Ti-2Al matrix has 100-hr creep-rupture strengths at 2000 and 2200°F (1093 and 1204°C) of 35,000 psi and 14,000 psi, respectively, in an inert gas environment. Comparison with the advanced nickel base alloy VIA on a density compensated basis (at a stress to density ratio of interest for buckets of 52,000 in.) indicates that the temperature to cause rupture in either 100 or 1000 hr is approximately 80 to 90°F (44 to 50°C) higher for the composite. Even stronger composite materials of this type can probably be achieved by use of improved refractory alloy wires of high-strength tungsten alloys such as described in Ref. 26.

Chromium Alloys

The potential advantages of chromium as an engine material stem from its high melting point (about 700°F or 389°C higher than nickel or cobalt), low density (about 20% less than that for nickel and cobalt), and higher elastic modulus (about 42 million psi at room temperature compared to about 30 million psi for nickel and cobalt). The major problems with chromium are its extreme brittleness at temperatures below about 300 to 500°F (149 to 260°C) and its reactivity with air or nitrogen at high temperatures. This can lead to even more severe embrittlement. Like most body-centered cubic metals chromium exhibits a ductile to brittle transition behavior. The ductile to brittle transition temperature (DBTT) may be below room temperature for high-purity chromium with a properly worked microstructure. However, it is commonly 300 to 500°F (149 to 260°C) for chromium of commercial purity or for worked or recrystallized chromium alloys having strength levels of interest for application to turbine blades or stator vanes of advanced air breathing engines. Moreover, prolonged exposure to air at temperatures above approximately 1500°F (816°C) can raise the DBTT to 1800°F (982°C) or higher. This severe embrittlement is due to both solution of nitrogen and the formation of a hard, brittle nitride layer on the surface. Nitrogen embrittlement is the biggest deterrent to the use of chromium alloys in turbojet engines.

Chromium Alloy Development

Prior to NASA's sponsorship of chromium alloy research in 1965, several alloys with attractive high-temperature strength had been identified. Foremost among these were alloy E (Cr-2Ta-0.5Si-0.1Ti) developed in Australia²⁷ and C207 (Cr-7.5W-0.8Zr-0.2Ti-0.1C-0.1Y) developed in the U. S.²⁸ The C207 alloy had a 100-hr rupture strength of 16,000 psi at 2000°F (1093°C), thus offering a temperature advantage of at least 100°F (55°C) over the strongest superalloys available at that time. Alloy E was less strong but considerably more ductile, having a ductile to brittle transition temperature below room temperature in the optimum condition.

In 1965, NASA's Lewis Research Center contracted with the General Electric Company's Flight Propulsion Division, developers of the alloy C207, to further develop chromium base alloys. Objectives of this program were to improve both high-temperature strength and low-temperature ductility and to increase resistance to both oxidation and nitrogen embrittlement at high temperatures. In general, emphasis was placed on the further development of complex carbide dispersion strengthened systems typified by the alloy C207. To date, over 200 chromium alloys have been melted and evaluated. The available results are presented in detail in Ref. 29 and are summarized below.

Five broad classes of alloy additions were included in this study: 1) nitridation inhibitors (Y, Th, La); 2) solid solution strengtheners (Mo, W, V); 3) solid solution ductilizers (Re, Ru, Co); 4) dispersion strengtheners (carbides, borides, intermetallics); 5) complex combinations of the foregoing.

Properties evaluated included:

1) Elevated temperature tensile strength in vacuum in both the wrought and recrystallized condition. For a few alloys, creep-rupture tests were run at 2100°F (1149°C) in helium.

Table 3 Stress-rupture properties of stress-relieved chromium alloys at 2100°F (1149°C)

Nominal composition, weight %	Stress, ksi	Life, hr	Elongation, %
Cr-7.1Mo-1.0Nb-0.09C-0.08Y	15.0	246.0	25.0
	17.5	62.2	38.4
Cr-7.1Mo-2.0Ta-0.09C-0.08Y	15.0	132.7	27.5
Cr-7.1Mo-0.5Ti-0.09C-0.08Y	15.0	80.1	32.1
Cr-7.1Mo-1.0Hf-0.5Zr-0.09C-0.08Y	15.0	19.8	32.2

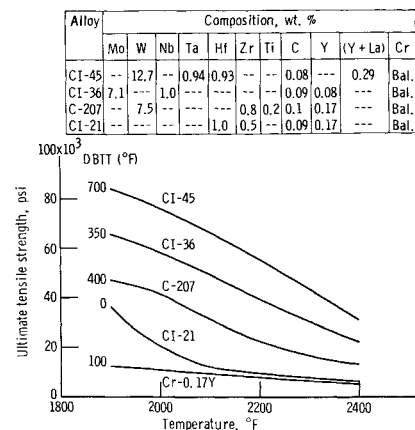


Fig. 6 Comparison of tensile properties of chromium alloys in the stress-relieved condition.

- 2) Ductile to brittle transition temperature in tension.
- 3) Air oxidation and nitridation behavior in the range 1500 to 2400°F (816 to 1316°C).

The major results of this study to date are summarized in the following.

1) The alloy with the best combination of high-temperature strength and low-temperature ductility is an alloy of composition Cr-7.1Mo-1.0Nb-0.09C-0.08Y (CI-36). As shown in Fig. 6, this alloy in the stress relieved condition combines a tensile strength at 1900°F (1038°C) of 65,000 psi with a DBTT of 350°F (177°C). From the limited data shown in Table 3, its 100 hr stress-rupture life at 2100°F (1149°C) is estimated to be about 17,000 psi. Comparison of the 1000-hr stress-rupture life of this alloy (extrapolated from shorter-time data) with that of the advanced nickel base alloy VI-A on a density compensated basis (at a strength/density ratio of about 52,000 in.) indicates a potential temperature advantage of approximately 200°F (111°C) for the chromium alloy.

2) The highest strengths were observed for the Cr-12.7W-0.94Ta-0.93Hf-0.08C-0.029 (Y + La) alloy (CI-45). This alloy had tensile strengths above 80,000 and 30,000 psi at 1900 and 2400°F (1038 and 1316°C), respectively. However, its DBTT was above 700°F (371°C). When compared at identical atomic percent levels, tungsten is a more potent solid solution strengthener for chromium than is molybdenum; however, it has a more adverse effect on workability and low-temperature ductility.

3) Several dilute carbide-containing or boride-containing alloys exhibited DBTT's below room temperature combined with tensile strengths in the wrought condition above 35,000 psi at 1900°F (1038°C). However, these ductile chromium alloys do not offer any temperature advantage over advanced nickel base superalloys at stress levels of interest for turbine blade application.

4) The oxidation and nitridation resistance in air of Cr-Y alloys containing Nb, Ta, and Ti carbide dispersions is markedly inferior to those with Hf-rich or Zr-rich carbide dispersions. Several HfC-containing alloys showed no nitridation and only slight internal hardening after 25-hr exposures as high as 2400°F (1316°C).

5) Additions of La or La + Y were more effective than Y alone in retarding nitridation of alloys with NbC, TaC, and TiC dispersions, at least through 100 hr at 2100°F. Although La and Y are very beneficial from the standpoint of oxidation and nitridation resistance, they have very low solubilities in carbide containing alloys. If not controlled to levels less than about 0.1 to 0.2%, they promote the formation of low melting eutectics which segregate to grain boundaries and impair the workability of these alloys.

6) Several noncarbide containing alloys exhibited outstanding resistance to nitridation in 25-hr exposures at 2400°F

Table 4 Summary of air oxidation behavior of selected, wrought chromium alloys

Alloy nominal composition, wt %	Re-tained Y + La, wt %	Temperature, °F, ^a °C	Total weight change, mg/cm ²	Nitride layer, mils	Depth hardened, mils
Cr-0.17Y	0.13	2100 (1149)	2.3	1 to 4	1 to 4
		2400 (1316)	10.6	2.5	4
Strong alloys					
Cr-12.7W-0.94Ta-0.93Hf-0.08C-0.29(Y + La)	0.04	2100 (1149)	28.3	4.5	17
		2400 (1316)	90.0	24	40
Cr-7.1Mo-1.0Nb-0.09C-0.08Y	0.05	2100	16.1	4	15
		2400	43.1	5 to 7	19
Ductile alloys					
Cr-1.0Hf-0.5Zr-0.09C-0.17Y	0.02	2100 (1149)	0.4	0	0
		2400 (1316)	18.5	12	14
Cr-12.8Re-0.93Ta-0.92Hf-0.08C-0.29(Y + La)	0.08	2100	1.8	0	5
		2400	24.2	0	4
Nitridation-resistant alloys					
Cr-0.17Hf-0.13Th-0.17Y	0.13	2100 (1149)	1.9	0	0
		2400 (1316)	1.9	0	0 to 1
Cr-66Re	^b	2100	3.2	0 to 4	0
		2400	6.2	0	0

^a 100-hr air exposure at 2100°F; 25 hr at 2400°F.^b Arc-melted alloy; no yttrium added.

(1316°C). As indicated in Table 4, the binary Cr-66 Re alloy showed no evidence of nitride layer formation or internal hardening after this exposure. Similarly, a Cr-0.17Hf-0.13Th-0.17Y alloy showed no nitride layer formation and only slight hardening to a depth of about 1 mil after the same exposure. The latter alloy is much too weak, whereas the high-rhenium alloy would be prohibitively expensive for use as a structural material. However, their excellent nitridation resistance suggests the use of such alloys as nitrogen barriers in the form of a thin surface cladding on a stronger alloy.

In summary, chromium alloys with attractive high-temperature strength are now available. The tensile DBTT of such alloys is well above room temperature, but may be only 350 to 400°F (177 to 204°C) in the optimum condition. Although good ductility at room temperature remains a goal of our chromium alloy research, we believe that it is unlikely that this can be achieved in high-strength alloys. The level of ductility achieved in the better alloys developed in this program may be adequate for turbine blades or stator vanes, since the DBTT's of these alloys are well below normal operating temperatures for these parts. The most critical problem that is yet to be solved is nitrogen embrittlement during high-temperature air exposure, since this can lead to DBTT's above 1800°F (982°C), clearly unacceptable for engine components.

Coatings for Chromium Alloys

Simultaneously with the chromium alloy programs described previously, NASA sponsored several research programs and conducted in-house research aimed at preventing nitrogen embrittlement by use of external surface coatings or claddings on a Cr-5W-0.05Y substrate. The approaches studied and an indication of the over-all scope of the program are as follows:

1) Aluminide coatings—Chromalloy Corporation³⁰: In this program, the protective capability of aluminide coatings deposited by pack cementation techniques was investigated. Coating systems studied included Al, Al-Fe, Al-Co, Al-Ti, Al-Fe-Co, Al-Co-Ti, Al-Fe-Ti and modifications of these.

2) Silicide coatings—Solar Division of International Harvester³¹: This program involved deposition of complex

silicides of Ti-Cr, Ti-Cr-V, and Ti-Mo over diffusion barriers of either vanadium or rhenium. Because of difficulties with the diffusion barriers, the capabilities of the silicides were not adequately determined.

3) Ductile claddings—Battelle Memorial Institute³²: The use of 5-mil foils of oxidation resistant alloys such as Ni-30Cr and Ni-20Cr-20W applied to the surface by hot-gas pressure bonding was investigated. Such clads were generally applied over tungsten or tungsten and platinum foil diffusion barriers.

4) Noble metal diffusion barriers—NASA Lewis Research Center³³: The use of electrodeposits of Pd and Pt as nitrogen diffusion barriers was explored.

Results of these investigations have not shown any of the systems investigated to have a high degree of promise. Although several of the systems showed excellent oxidation resistance at 2100°F (1149°C), and were effective in preventing nitride formation on the Cr-5W-0.5Y substrate, embrittlement resulted from other causes. The causes of embrittlement in all cases have not been established; however, solution hardening by diffusion of nickel or aluminum into the substrate appeared at least partially responsible. The diffusion barriers used, including W, Pt, V, and Re were generally unsatisfactory in varying degrees. It is apparent that new and different approaches to overcoming the problem of nitrogen embrittlement of chromium alloys need to be explored.

Coatings for Refractory Metals

Because of their high melting points and good high-temperature strength, alloys of the refractory metals tungsten (W), tantalum (Ta), molybdenum (Mo), and niobium (Nb) have frequently been considered for use in aircraft gas turbine engines. However, all of these metals oxidize rapidly at temperatures above 1500°F (816°C). Although oxidation resistance can be improved by alloying, even the most oxidation resistant alloys fall far short of meeting the requirements of gas turbine operation. Thus, the use of protective coatings appears to offer the only hope for providing suitable oxidation resistance. Unfortunately, coatings for refractory metals have generally not demonstrated the high degree of reliability required for aircraft engine use.

In 1965, NASA engineers reviewed possible opportunities for utilizing refractory metals in advanced turbojet engines and concluded that the use of coated tantalum alloys for stator vanes merited additional consideration.²¹ The stator vane application was viewed as being more promising than the rotating bucket application in which failure of one bucket due to local coating defects could cause severe damage to other buckets or engine components. Tantalum alloys had received very little study for aircraft engine use but the relatively high melting point of the oxide of tantalum (above 3400°F, 1871°C), suggested that difficulties encountered in other refractory alloy systems with low melting or volatile oxides might be less severe for tantalum alloys. Further, tantalum alloys with suitable strength and fabricability for stator vane application had already been developed. One of these, T-222 (Ta-9.6W-2.4Hf-0.01C), appeared to have adequate strength for vane use at temperatures up to at least 2400°F (1316°C), and was therefore selected as the substrate material for a program to develop oxidation resistant coatings for tantalum alloy nozzle vanes.

Significant progress has been made by the contractor, Solar Division of International Harvester Company, in developing a group of silicide coatings based on tungsten, molybdenum, vanadium, and titanium.³⁴ These coatings are applied by a two-step process. First, a modifier layer consisting of tungsten, molybdenum, vanadium, and titanium metal powders suspended in a suitable carrier is applied by slurry techniques and is partially sintered in vacuum. This relatively porous coating is then silicided by pack cementation in argon to form a mixture of silicides. Excess silicon deposited in the pores of the modifier layer appears to contribute to the oxidation resistance of these coatings.

The most oxidation resistant coating developed to date has a modifier layer of composition 35Mo-35W-15V-15Ti. After siliciding, this coating reproducibly protected specimens of the T-222 alloy for 600 hr at both 1600°F (871°C) and 2400°F (1316°C)²⁴ during cyclic exposure to static air. One sample survived 1064 hr of furnace oxidation at 2400°F (1316°C). This is viewed as a significant advance in the state-of-the-art of coatings for tantalum alloys since prior to this development the best available coatings provided only 30 to 50 hr of protection in the same temperature range.

Studies are currently underway to optimize the composition of this coating system and to further evaluate such coated tantalum alloys in burner rigs which more closely simulate aircraft engine operating conditions. The potentially serious problem of impact damage such as might result from a foreign object passing through the engine is being investigated and attempts will be made to modify the coating, as necessary, to promote self-healing of parts subject to such damage.

Concluding Remarks

Over the past several years, NASA has conducted an extensive in-house and contractual program to develop improved materials for advanced air breathing engines. Considerable progress has been made in several areas. Of most immediate importance is the development of an advanced cast nickel base alloy, NASA-TRW VI-A. This alloy shows approximately a 50°F (28°C) improvement in use temperature over the strongest superalloys currently in use. Even larger improvements over the strengths of currently used superalloys have been achieved in chromium alloys and metal-matrix composite materials. However, many problems remain to be solved before the opportunities indicated by these latter developments can be utilized in aircraft engines. Foremost among the needs at this time is that for improved oxidation, nitridation, and erosion resistant coatings to permit use of these stronger materials at temperatures consistent with their strength potential.

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