NASA TECHNICAL MEMORANDUM
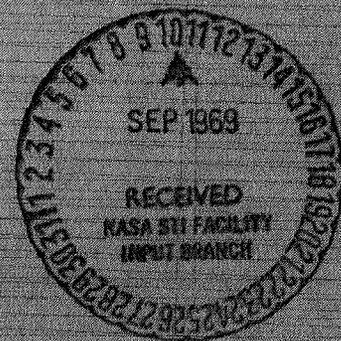
RECENT DEVELOPMENTS IN CHROMIUM AND CHROMIUM ALLOYS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1969

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ABSTRACT

Recent developments in chromium pertinent to its potential use in advanced jet engines are reviewed. Although chromium has a strength-to-density advantage over nickel, its inherent brittleness and further embrittlement by nitrogen during high-temperature exposure are serious limitations to its use. Twelve chromium alloys are currently under development, the strongest showing a potential 150° F (83 K) service temperature advantage over nickel-base superalloys. However, a better balance between solution strengthening and precipitate strengthening must be achieved in order to improve the low temperature ductility of these alloys. Improved coatings for protection against nitrogen embrittlement must be developed.

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SUMMARY

Chromium-base alloys, which have been under study now for slightly more than two decades, are attractive as potential competitors for nickel alloys for high temperature applications in advanced jet engines. Although chromium has a strength-to-density advantage over nickel, it is normally brittle at room temperature and is further embrittled by nitrogen during high temperature air exposure.

The high temperature strength of chromium can be increased threefold to fourfold by solution strengthening with elements such as tantalum, columbium, tungsten, molybdenum, and rhenium. Solution strengthening, however, involves a significant increase in the ductile-brittle transition temperature. Similar or larger improvements in the strength of chromium can be achieved by precipitate strengthening with borides, carbides, and nitrides of the Groups IVa and Va elements. These precipitates do not embrittle chromium to the same extent as do solution strengthening additions and may even be ductilizing. Coarsening rate estimates suggest that carbides at least should retain sufficiently fine sizes as to be strengthening for times of 1000 hours or longer at 2000° to 2200° F (1366 to 1478 K).

Nitrogen is particularly deleterious to the ductility of chromium because of its high solubility at elevated temperatures and the nature of the Cr_2N precipitate. Nitrogen embrittlement of chromium during high temperature exposure can be reduced by rare earth alloying, but the effectiveness of these additions is reduced on further alloying for high temperature strength.

A total of twelve chromium alloys can be classified as recently developed or currently under development. These include five from the United States, three from Australia, and four from the Soviet Union. The strongest of these alloys offer up to a 150° F (83 K) temperature advantage over nickel alloys but the impact ductile-brittle transition temperatures are high.

Future work on chromium should include further development of protective coatings or surface alloying techniques to reduce nitrogen embrittlement and emphasis on dispersion strengthening to achieve a better balance between high temperature strength and low temperature ductility.

INTRODUCTION

Chromium-base alloys are currently of considerable interest as potential turbine bucket and stator vane materials for advanced jet engines. The advantages of chromium over current nickel-base superalloys are well-known and include higher melting point, higher elastic modulus, and lower density. The disadvantages of chromium are equally well-known, being primarily the transition from ductile to brittle behavior, usually above room temperature, a characteristic shared with its sister elements molybdenum and tungsten, and the further embrittlement resulting from nitrogen contamination during high temperature air exposure.

Historically, chromium as an alloy base has been of interest for slightly more than two decades, dating back to the work of Parke and Bens in the middle 1940's (ref. 1). These early studies were hampered by the unavailability of chromium metal of good purity, the only available grade at that time being electrolytic chromium of questionable quality.

The extensive studies on chromium in Australia initiated in 1946 (ref. 2) and the development of the iodide process for the production of high-purity chromium in the early 1950's (ref. 3) provided major impetus to the development of chromium-base alloys. Concurrently, nitrogen was identified as the major embrittling impurity in chromium (ref. 4).

The 1955 Conference on Ductile Chromium and Its Alloys (ref. 5) represents a milestone in the development of usable chromium-base materials. At this meeting, the effects of purity on ductility and the results of early alloying studies on strength (refs. 6 and 7) were reported.

From 1955 to 1959, chromium research continued through a number of largely unrelated projects. The only identifiable continuing effort during this time period was that jointly conducted by the Aeronautical Research Laboratories and the Defence Standards Laboratory, both of the Research and Development Branch of the Australian Department of Supply.

In 1959, the beneficial effects of yttrium on the oxidation/embrittlement resistance of chromium were reported by Collins and coworkers from the General Electric Company (refs. 8 and 9). This discovery and the development of ductile Cr-MgO alloys by Scruggs and coworkers at the Bendix Corporation (ref. 10) marked the initiation of a second period of alloy development which is still continuing. The early Bendix alloy, Cr-6MgO-0.5Ti, was designated Chrome-30 (ref. 11). Development of Cr-MgO alloys has continued under sponsorship of the Air Force and the Bureau of Naval Weapons, culminating in the recent development of the Chrome-90S alloy (ref. 12).

Alloy development at the General Electric Company was conducted under partial Air Force sponsorship and resulted in the development of the C-207 alloy, Cr-7.5W-0.8Zr-

0.2Ti-0.1C-0.15Y, reported by Clark and Chang in 1966 (ref. 13). Development of these alloys combining both carbide strengthening and solid solution strengthening has continued since 1965 under NASA sponsorship.

The Australian efforts resulted in the development of Cr-2Ta-0.5Si-0.1Ti, designated as Alloy E, in the early 1960's (ref. 14). Modified alloys, designated as H and J, were reported subsequently (refs. 15 and 16), with the major portions of this extensive and valuable program terminating in 1965.

This report reviews the reasons for our continuing interest in chromium alloys, the pertinent physical metallurgy of chromium including the general effects of alloying, and the status of chromium alloys currently under development. Suggested areas for future research are also discussed. For a more detailed reveiw of chromium technology up to 1966, the reader is referred to the comprehensive report by Maykuth and Gilbert (ref. 17). The articles by Sims (ref. 18), Wain and Johnstone (ref. 15), and Rogers and Brown (ref. 19), and the recently revised book by Sully (ref. 20) also provide excellent background information.

METHODS FOR OBTAINING HIGHER OPERATING TEMPERATURES IN JET ENGINES

Much of the current interest in chromium alloys is motivated by their potential for use in advanced aircraft engines. Therefore, before reviewing the properties of chromium, it is appropriate to consider briefly the status of competitive materials and methods for obtaining higher operating temperatures.

The stress-to-density ratios for rupture in 1000 hours are shown in figure 1 for typical nickel-base superalloys. The horizontal bands indicate the stress levels typical of rotating turbine buckets and stator vanes in many modern engines. The current cast alloys, such as IN-100 and the NASA-TRW-VIa alloy, offer an operating temperature advantage of about 100° F (56 K) over wrought alloys, such as U-700.

Currently, turbine inlet temperatures above the temperature capabilities of nickel-base alloys are being achieved by cooling the nickel components with air bled from the aft section of the compressor. This involves a penalty in terms of a slight loss of expensive compressor air and increased engine complexity. It would be more desirable to use a high temperature material which did not require cooling.

Several potential materials for achieving higher operating temperatures are being studied. In addition to chromium, these include improved nickel alloys, single-crystal alloys, thoria-dispersed nickel and cobalt alloys, fiber-reinforced alloys, and at much higher temperatures, columbium and tantalum alloys. All of these materials are currently receiving attention and are competitive with chromium as potential high tem-
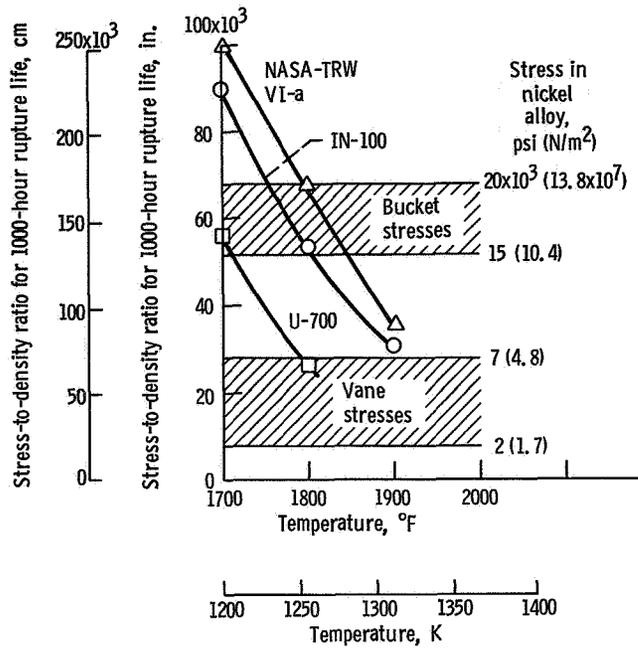
Figure 1. - Current status of materials for tur-
bine components.

TABLE I. - PROPERTIES OF CHROMIUM AND NICKEL

	Chromium	Nickel
Structure	Body-centered cubic	Face-centered cubic
Melting point, $^{\circ}F$ (K)	3410 (2150)	2650 (1728)
Modulus, psi (N/m^2)	36×10^6 (2.5×10^{11})	30×10^6 (2.1×10^{11})
Density, lb/in.^{3} (g/cm^3)	0.26 (7.19)	0.322 (8.9)
Coefficient of thermal expansion, F^{-1} (K^{-1})	3.4×10^{-6} (6.2×10^{-6})	7.4×10^{-6} (13.3×10^{-6})
Low temperature ductility	Poor	Good
Oxidation resistance	Embrittles in air	Fair
Vapor pressure at 2000° F (1366 K), mm Hg (N/m^2)	2×10^{-5} (2.7×10^{-3})	2×10^{-6} (2.7×10^{-4})

erature engine materials.

Table I lists the major properties of interest for both chromium and nickel. Chromium has the open, body-centered-cubic structure and thus is expected to have higher self-diffusion rates and lower creep strength at the same homologous temperature as nickel, which has the close-packed face-centered-cubic structure. However, the open structure of chromium is more than compensated for by its higher melting point, higher elastic modulus, and lower density, which combine to give chromium a significant strength-to-density advantage over nickel. Chromium has a lower coefficient of thermal expansion than nickel, making chromium more resistant to thermal fatigue during cyclic heating.

The major disadvantages of chromium are its almost complete lack of ductility below the ductile-brittle transition temperature, which for unalloyed recrystallized chromium of commercial purity is around 300° F (422 K), and the further severe embrittlement which results from nitrogen contamination during high temperature air exposure. In contrast, nickel exhibits good ductility and toughness to subzero temperatures.

The high vapor pressure of chromium is of some concern during melting and during vacuum heating, such as for use in space applications, but has not been shown to be deleterious during normal air heating.

GENERAL ALLOYING EFFECTS ON STRENGTH AND DUCTILITY

In order to present an adequate picture of the present status of chromium alloy development, it is necessary to assess as best as possible the effects of individual alloying elements of interest on the pertinent properties of chromium. These properties, for the purposes of this review, include high temperature strength, particularly creep strength, low temperature ductility, and oxidation-nitridation resistance.

The effects of solid solution alloying on the high temperature strength of chromium are presented in figure 2 (refs. 14 and 21 to 26). In order to construct this figure, it has been necessary to draw from a number of separate investigations, most of which differed significantly in the manner of alloy preparation and also in the reporting of strength in terms of tensile or creep results. For this reason, it was chosen to report the strengthening effects as a ratio of the tensile or creep strength to that of unalloyed chromium under similar conditions.

It is seen from figure 2 that substitutional solutes can increase the high temperature strength of chromium threefold to fourfold. The highest specific strengthening rates are achieved on alloying with the Group Va elements, Ta, Cb, and V. Tantalum, and probably also columbium, lose their strengthening effectiveness at low alloying levels because of restricted solubilities in chromium, both of which are in the range of 0.5 to 1 atomic
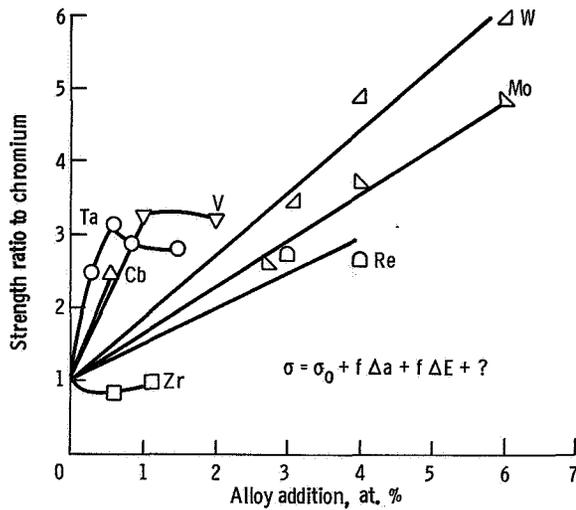
Figure 2. - Effects of substitutional solutes on strength of chromium (1800° to 2400° F; 1255 to 1589 K).

percent in the temperature range of interest. Vanadium also appears to become less effective at alloying levels above 1 atomic percent, although it is completely soluble in chromium. Of the Group VIa solutes, tungsten is a more effective strengthener than molybdenum and both are more effective than rhenium from Group VIIa. These three elements have more extended solubilities in chromium than do tantalum and columbium, but alloys containing 4 atomic percent or more of these elements are difficult to fabricate. Zirconium, the lone representative of Group IVa for which data were available, is seen to be weakening.

The relative strengthening rates of solutes within Group Va and within Groups VIa and VIIa follow qualitatively the well-known principles of solution strengthening which relate strengthening effectiveness to differences in atomic size and elastic modulus. The most effective strengtheners in these two groups, tantalum and tungsten, have the largest size differences and the largest elastic moduli differences with chromium. An additional unknown factor, probably related to the position of the solute in the periodic table, is needed to correlate the strengthening effects of solutes from different periodic groups.

Unfortunately, most solution strengthening solutes have a deleterious effect on the low temperature ductility of chromium (refs. 21, 25, 27 to 31). (Exceptions are Fe, Co, Re, and Ru, which at large alloying concentrations promote improved ductility through the "rhenium ductilizing effect" (ref. 32).) Representative data on the effects of these elements on the ductile-brittle transition temperature of chromium are shown in figure 3. These data, taken from the study of Carlson et al. (ref. 30), illustrate the changes in ductile-brittle transition temperature on alloying with columbium, tantalum, molybdenum, and tungsten. The increases in ductile-brittle transition temperatures on alloying with
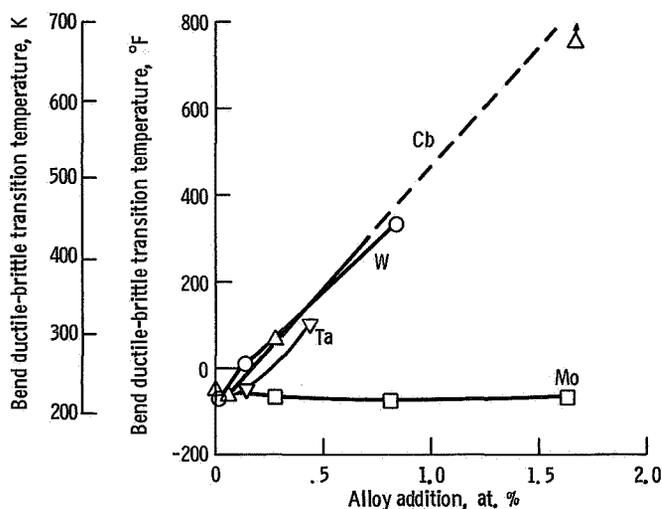
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Figure 3. - Effects of substitutional solutes on ductile-brittle transition temperature of chromium.

these four elements may be considered typical of the effects of alloying with solution strengthening elements. Although molybdenum had little effect in this study, other work (refs. 25 and 29) indicates it to be almost as embrittling as tungsten. It is thus apparent that although considerable strengthening can be achieved in chromium by alloying with substitutional solutes, such strengthening is only achieved at the cost of a significant increase in the ductile-brittle transition temperature.

The low transition temperature of -50° F (228 K) for unalloyed chromium was observed in Carlson's study because of the slow bending rate used. It is of interest to note that minor solution softening effects were observed at alloying levels of about 0.05 atomic percent.

Limited data on the effects of precipitate strengthening with carbides, borides, and nitrides are presented in figure 4 (refs. 15, 23 to 26, and 33 to 38). In this case, as for solid solution strengthening, it is necessary to present the results as strength ratios to unalloyed chromium in order to compare results obtained by different investigators at different temperatures. For all precipitate alloys, the interpolated or extrapolated strengths for rupture in 100 hours were used.

Among the carbides, it is seen that least strengthening is obtained from ZrC, while much higher strength increments are obtained from CbC and from TaC. This difference is related to the low solubility for zirconium in chromium, which prevents refinement of the carbides through solutioning and results in the retention of coarse carbides which are less strengthening (ref. 38).

The most effective precipitate strengthener for which data are available is TaB_2, which produces almost a fivefold increase in the creep strength of chromium. Columbium boride and other mixed borides are also known to be effective creep strengtheners for
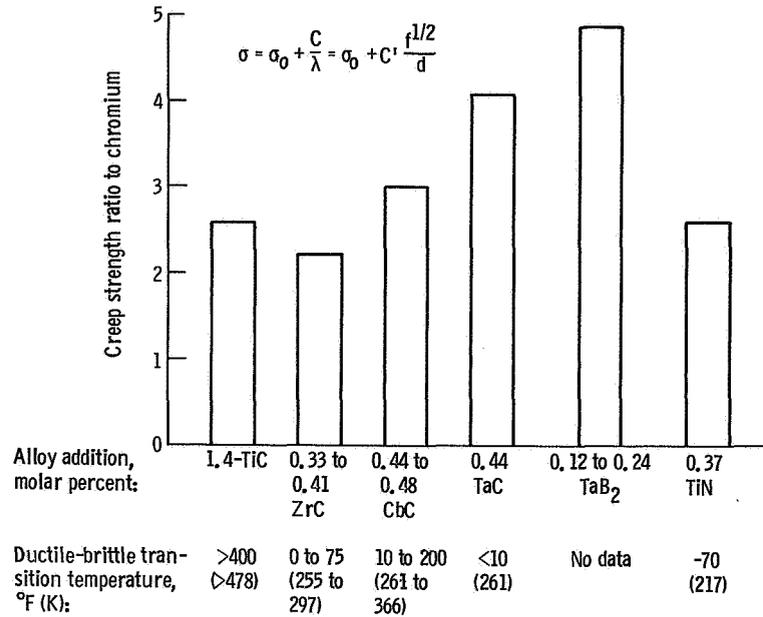
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chromium from the recent work of Clark (ref. 25).

Titanium nitride is seen to be a moderate strengthener for chromium and also promotes a low ductile-brittle transition temperature.

The strength of a precipitate-strengthened or dispersion-strengthened material is related to the particle spacing, according to Orowan (ref. 39), Ansell (ref. 40), and others, by

$$\sigma = \sigma_0 + \frac{C}{\lambda} \tag{1}$$

where

σ yield strength or creep strength

σ_0 matrix strength

C constant including Burgers vector and matrix shear modulus

λ interparticle spacing

Westmacott et al. (ref. 41) have shown by planar analysis that λ is directly proportional to the particle diameter d and inversely proportional to the square root of the volume fraction of dispersed phase f, so that equation (1) can be written as

$$\sigma = \sigma_o + C' \frac{f^{1/2}}{d} \tag{3}$$

Thus, decreasing the particle size at a constant volume fraction or increasing the volume fraction at a constant particle size tends to increase the strength contribution from the second phase. Recent data on tungsten and W-Re strengthened by HfC (ref. 42) tend to confirm the validity of equation (3). Ryan (ref. 36) has also shown that the creep strength of chromium strengthened by TaC is decreased by increasing the TaC particle size. Considerable work, however, remains to be done on chromium in order to identify the most strengthening precipitate and determine the optimum volume fraction and particle size.

It is most significant to note that precipitate strengthening does not increase the ductile-brittle transition temperature to the extent that solution strengthening does. As indicated in figure 4, the range of transition temperatures is equal to or less than that of unalloyed chromium. The work of Ryan, in fact, indicated that the carbides of most of the Group IVa and Va elements reduced the transition temperatures to significantly below that of unalloyed recrystallized chromium. These results are in accord with the recent theories of Hahn and Rosenfield (ref. 43) and others (ref. 44), regarding the ductilizing of Group VIa metals by finely dispersed second phases.

Thus, strength improvements in chromium comparable to those achieved by solution strengthening can be obtained by proper dispersion strengthening without a concurrent increase in the ductile-brittle transition temperature.

The question of particle size stability must be considered when developing alloys whose strength is dependent on the maintenance of a fine particle size. Recent work on the coarsening of a precipitated phase in a binary system has shown that the coarsening rate is cubic with respect to time and is proportional to both the diffusivity and the soluble concentration of the slower-diffusing component (ref. 45). It may thus be estimated that for ternary systems, such as carbides of the Group IVa and Va elements in a Group VIa matrix, the coarsening kinetics should also be cubic and should be proportional to the diffusivities and soluble concentrations of the Group IVa or Va element. In order to examine the coarsening rates of carbides in chromium on this basis, cubic coarsening rates were estimated from the data of Ryan (ref. 36) (the experimental coarsening curves were approximately parabolic at 2372° and 2552° F (1573 and 1673 K) and logarithmic at 2192° F (1473 K)) and are compared with carbide coarsening rates in molybdenum (ref. 46) and tungsten (ref. 42) in figure 5. The similarity of the coarsening rates and of the temperature dependency on a homologous temperature basis suggests that the diffusivity of the carbide forming element, which would have a temperature dependence similar to that for self-diffusion of the solvent metal, is rate-controlling. More importantly, however, Ryan's data indicate that CbC and TaC precipitates in chromium should be able to main-
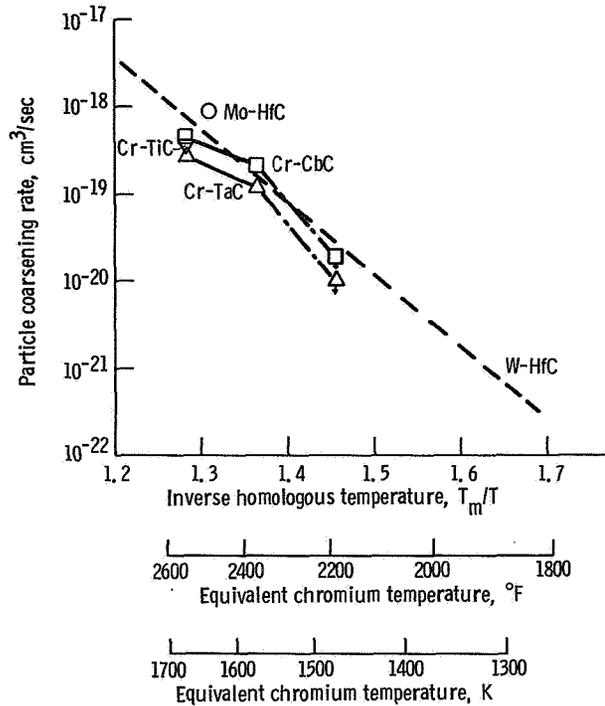
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Figure 5. - Coarsening rates of carbides in chromium, molybdenum, and tungsten.

tain particle sizes of several tenths of a micron for times greater than 1000 hours in the temperature range of 2000° to 2200° F (1366 to 1478 K). Good creep strength should also be maintained in this time-temperature range.

EFFECTS OF NITROGEN ON DUCTILITY

It is now well-known that nitrogen has a particularly deleterious effect on the ductility of chromium. This effect poses a serious obstacle to the development of useful chromium alloys, since the oxide scale which forms during high temperature air exposure is usually sufficiently porous that nitrogen can saturate and embrittle the surface of the underlying substrate.

Part of the reason for the rather unusual sensitivity of chromium to nitrogen as opposed to oxygen lies in the relatively high solubility of nitrogen in chromium at elevated temperatures. As shown in figure 6, carbon has a fairly high solubility in all three Group VIa metals, up to about 1 atomic percent (refs. 47 and 48). In contrast, oxygen solubility is low, less than 0.05 atomic percent in all three metals (refs. 49 to 51), possibly reflecting the larger diameter of the interstitially dissolved oxygen ion. Nitrogen solubility, however, ranges from less than 0.01 atomic percent in tungsten to 1 atomic
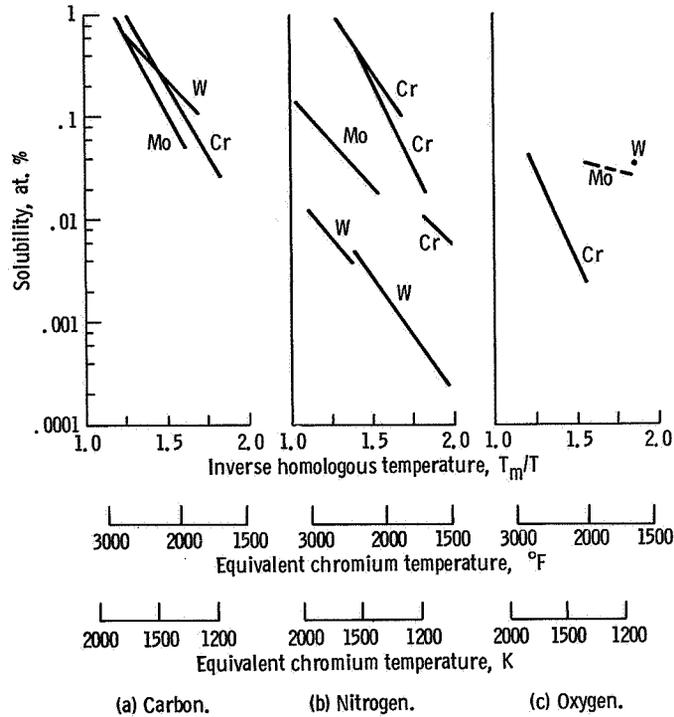
Figure 6. - Interstitial solubilities in chromium, molybdenum, and tungsten.

(a) Carbon.   (b) Nitrogen.   (c) Oxygen.

percent in chromium (refs. 49 and 52 to 56). Thus, at high temperatures, chromium can dissolve about 100 times as much nitrogen as oxygen. This high solubility, plus the fact that the nitride tends to precipitate as an acicular intragranular phase rather than as a spheroidal or intergranular phase like the carbide and oxide, makes nitrogen more deleterious than oxygen in chromium.

The effects of nitrogen on the ductility of chromium have been the subject of several recent investigations (refs. 4 and 57 to 60). The data plotted in figure 7 are illustrative of the results. When dilute chromium-nitrogen alloys are slow-cooled, the nitride can coalesce into large particles which increase the ductile-brittle transition temperature by only about 100° F (56 K) at the 0.1 atomic percent nitrogen level. However, as the cooling rate increases, the effectiveness of nitrogen in increasing the ductile-brittle transition temperature also increases. Although it was originally postulated that this increased effect was a result of nitrogen retained in supersaturated solution, the effect is now attributed to a decrease in size of the nitride precipitate, possibly through increased coherency strains between the precipitate and the chromium matrix (ref. 61). Gilbert and Klein (ref. 62) have recently shown that dissolved nitrogen, which can be retained in solution only by rapid quenching of thin sections, has little effect on the transition temperature of chromium. It may also be noted in figure 7 that the "unalloyed" iodide chromium of Cairns and Grant also exhibited an effect of quenching rate on ductile-brittle transition temperature, suggesting that high purity chromium is quite sensitive to trace impurities.
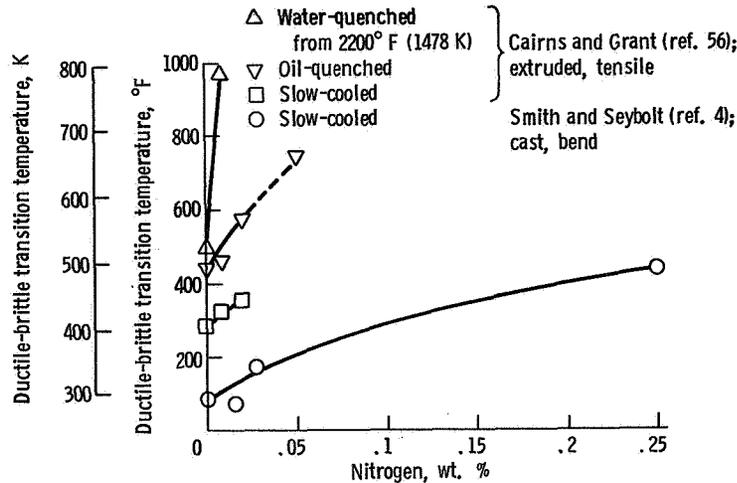
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Figure 7. - Effects of nitrogen on ductile-brittle transition temperature of chromium.

The effects of alloying on the oxidation behavior of chromium has been the subject of several recent studies (refs. 15, 22, 25, 38, and 63 to 70). The results of these studies, however, have usually been expressed in terms of alloying effects on oxidation weight gain. As shown by Abrahamson and Grant (ref. 65), the oxidation weight gains cannot be related to nitrogen absorption nor presumably to the property of most interest, ductile-brittle transition temperature.

Some of the recent results of Clark (ref. 25) are directly pertinent in that the ductile-brittle transition temperatures (15° bend at 0.05 in./min (0.13 cm/min)) were measured as a function of both alloying and oxidation. These results are shown in figure 8. Although unalloyed chromium is not shown here, it has a bend transition temperature (90° bend at 1 in./min (2.5 cm/min)) of about 300° F (422 K) in the annealed condition and 1000° F (811 K) after air exposure for 100 hours at 2100° F (1422 K) (unpublished work, J. R. Stephens, NASA). The addition of 0.1 atomic percent yttrium is beneficial in reducing the transition temperature of chromium both in the annealed condition and after oxidation at 1500° and 2100° F (1089 and 1422 K) for 100 hours. This effect is shared by most of the other rare earths, notably lanthanum, and is apparently related both to gettering of interstitials from solution in chromium (ref. 71) and to promoting formation of a tightly adherent oxide scale which substantially reduces ingress of nitrogen to the substrate (ref. 64). Similar but more complex alloys, such as Cr-Y-Hf-Th, have been shown (refs. 22 and 25) to be even more resistant to oxidation/nitridation than Cr-Y and may be useful as claddings for a high strength substrate. Yttrium, however, is slightly detrimental to high temperature strength and, more unfortunately, is not so effective in reducing oxidation embrittlement of carbide-strengthened chromium alloys. Chromium-yttrium alloys with TiC, CbC, and TaC are seen in figure 8 to be particularly embrittled by high temperature
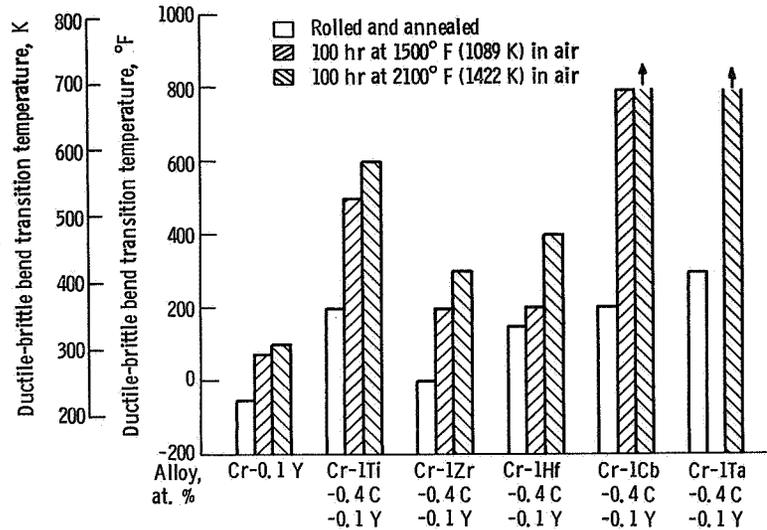
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Figure 8. - Effects of alloying on oxidation-embrittlement of chromium.

air exposure, while alloys with ZrC and HfC are not so prone to oxidation-embrittlement.

It is apparent that nitrogen embrittlement during high temperature air exposure poses a major problem to the development of chromium alloys. This problem does not appear amenable to solution by alloying, such as with yttrium. Protective coatings, clads, or special surface alloying techniques must be developed if chromium alloys are to be useful at high temperatures in air.

CURRENT CHROMIUM ALLOYS

A total of twelve chromium alloys can be classified as recently developed or currently under development. These include five from the United States, three from Australia, and from the Soviet Union. Compositions (where known) and developing organizations are given in table II.

The strength and ductility properties of the five United States alloys are summarized in figure 9 (refs. 12, 13, and 25). This group can be divided into two subgroups. Two alloys, designated C-207 and CI-41, are produced by induction melting and combine solution strengthening by tungsten or molybdenum with precipitate strengthening by carbides. These two alloys also contain small amounts of yttrium or yttrium plus lanthanum for scavenging and slightly improved oxidation resistance. Both alloys have good strength in the 2000° to 2100° F (1366 to 1422 K) range, with the CI-41 alloy exhibiting about a 100° F (56 K) service temperature advantage over C-207. Both alloys have moderately high ductile-brittle transition temperatures, particularly in impact, probably resulting

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TABLE II. - CHROMIUM ALLOYS UNDER DEVELOPMENT

Country	Designation	Composition, wt. %	Organization
United States	C-207	Cr-7. 5W-0. 8Zr-0. 2Ti-0. 1C-0. 15Y	General Electric (USAF)
	CI-41	Cr-7. 1Mo-2Ta-0. 09C-0. 1(Y+La)	General Electric (NASA)
	Chrome-30	Cr-6MgO-0. 5Ti	Bendix (Navy)
	Chrome-90	Cr-3MgO-2. 5V-0. 5Si	Bendix (Navy)
	Chrome-90S	Cr-3MgO-2. 5V-1Si-0. 5Ti-2Ta-0. 5C	Bendix (Navy)
Australia	Alloy E	Cr-2Ta-0. 5Si-0. 1Ti	Dept. of Supply
	Alloy H	Cr-2Ta-0. 5Si-0. 5Re	Dept. of Supply
	Alloy J	Cr-2Ta-0. 5Si	Dept. of Supply
Soviet Union	BX-2	Unknown	----------------------
	BX-2I	BX-2 plus Y	----------------------
	BX-3	Unknown	----------------------
	BX-4	Unknown	----------------------

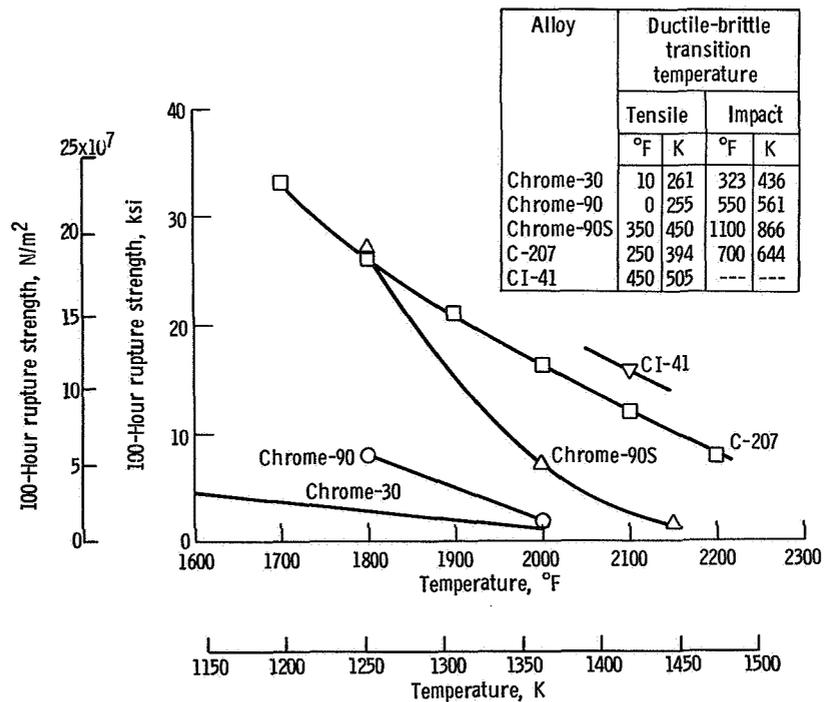| Alloy	Ductile-brittle transition temperature			
	Tensile		Impact	
	°F	K	°F	K
Chrome-30	10	261	323	436
Chrome-90	0	255	550	561
Chrome-90S	350	450	1100	866
C-207	250	394	700	644
CI-41	450	505	---	---

Figure 9. - Strength and ductility of United States chromium alloys.

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from alloying with tungsten and molybdenum. Both alloys have been produced as 100-pound (45-kg) induction-melted ingots. The CI-41 alloy has been fabricated to rod, plate, and sheet for use as a substrate for protective coatings development and for other special property evaluations (ref. 72).

The three alloys designated Chrome-30, Chrome-90, and Chrome-90S are produced by powder metallurgy techniques, the principal alloy addition in each being MgO. The Chrome-30 alloy, developed in 1962, also contains 0.5 percent titanium, while later alloys also contain other elements for improved high temperature strength and oxidation resistance. The main advantage of these alloys is the improved low temperature ductility and high temperature oxidation resistance imparted by MgO. As seen in figure 9, the Chrome-30 and Chrome-90 alloys exhibit tensile ductility at room temperature, but have low strength at elevated temperatures. The Chrome-90S alloy has improved high temperature strength, but at the expense of a substantial increase in the ductile-brittle transition temperature. This class of alloys may be useful in low strength applications such as stator vanes.

Three alloys have been developed under the auspices of the Australian Department of Supply, designated as E, H, and J. All have similar compositions based on Cr-2 Ta-0.5Si, with E and H also containing 0.1 percent Ti and 0.5 percent rare earth elements, respectively. The mechanical properties of alloy E have been studied rather extensively (refs. 15 and 73), but very little property data are available on alloys H and J. The high temperature rupture strength of alloy E is shown in figure 10 and is seen to be slightly lower than that of C-207 and CI-41. Both strength and ductility of alloy E are affected by annealing treatments, the ductility tending to increase and the rupture strength tending to decrease with increasing annealing temperature. In the as-extruded condition, alloy E has a bend transition temperature of about 200° F (366 K), but annealing at 2300° F (1533 K) reduces the transition temperature to -100° F (200 K). Alloy H has better ductility retention after high temperature air exposure than alloy E through the substitution of rare earth elements for titanium.

Advanced rig testing has been performed on all three of the Australian chromium alloys. Turbine buckets forged of alloys E and H withstood 9 hours of running at 1875° F (1297 K) in a rotating rig turbine wheel (ref. 74). The test was terminated when the combustor failed and pieces from the combustor caused two of the six chromium alloy buckets to fail at the root. Although the chromium alloy buckets showed considerably less creep extension than did the cobalt HS31 alloy buckets, the mode of failure indicates that the chromium buckets were brittle in impact at the root temperature. Clearly, chromium alloys must be ductile in impact at the minimum operating temperature in order to be used safely.

Several alloy J blades were also evaluated in a "cascade rig," which involved stationary heating to 2000° F (1366 K) for 25 hours in a sonic velocity gas stream (ref. 16). The major result from this test was the observation that the oxide scale was more adherent
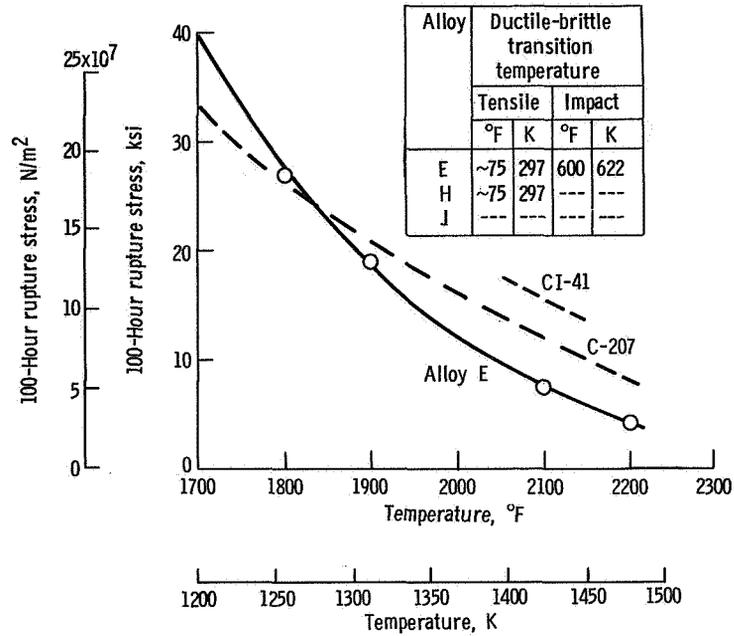
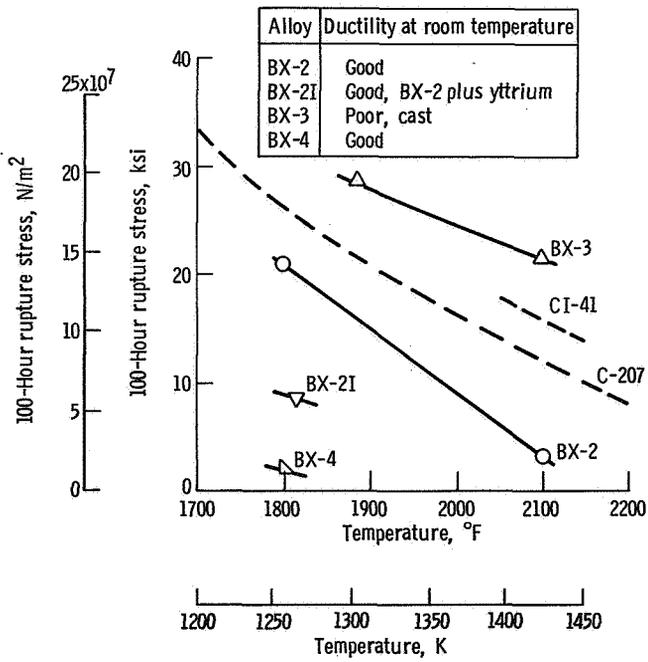Figure 10. - Strength and ductility of Australian chromium alloys.

Figure 11. - Strength and ductility of Soviet chromium alloys.

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and the depth of nitrogen contamination was considerably less after heating in the sonic velocity gas stream than after comparable heating in static air. Thus, static air exposure tests on chromium alloys may give inaccurate results (see also ref. 75).

The limited strength and ductility data available for Soviet alloys are summarized in figure 11 (refs. 76 and 77). The BX-3 alloy is apparently stronger than C-207 and CI-41, but is produced only in the cast condition and has poor ductility. The weaker BX-2, BX-2I, and BX-4 alloys are fabricable __ _ave "good" low temperature ductility. Compositions and status of development for these alloys are unknown.

The trade-off between high temperature strength and low temperature ductility for chromium alloys under development is indicated in figure 12. The data are seen to fall into two groupings, one comprised of the melted alloys, and the second comprised of the powder metallurgy alloys. The melted alloys have higher 2000° F rupture strengths than do the powder metallurgy alloys. It is also obvious that the major trend within each grouping is for the ductile-brittle transition temperature to increase substantially as the high temperature strength is increased. This is a result of reliance on solid solution strengthening for the major portion of the strength of these alloys. It is apparent that other means for strengthening, such as precipitate strengthening or dispersion strengthening, must be more effectively utilized in order to develop chromium alloys with a more usable combination of low temperature ductility and high temperature strength.
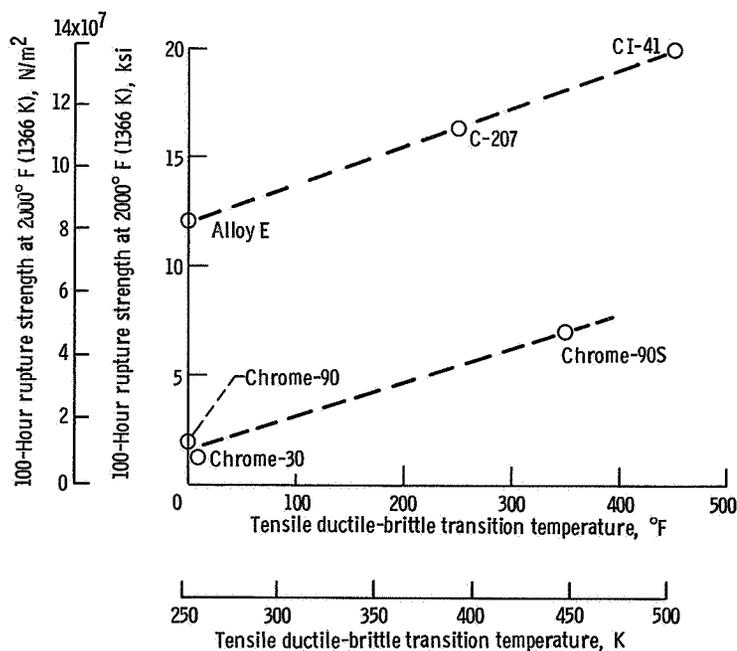

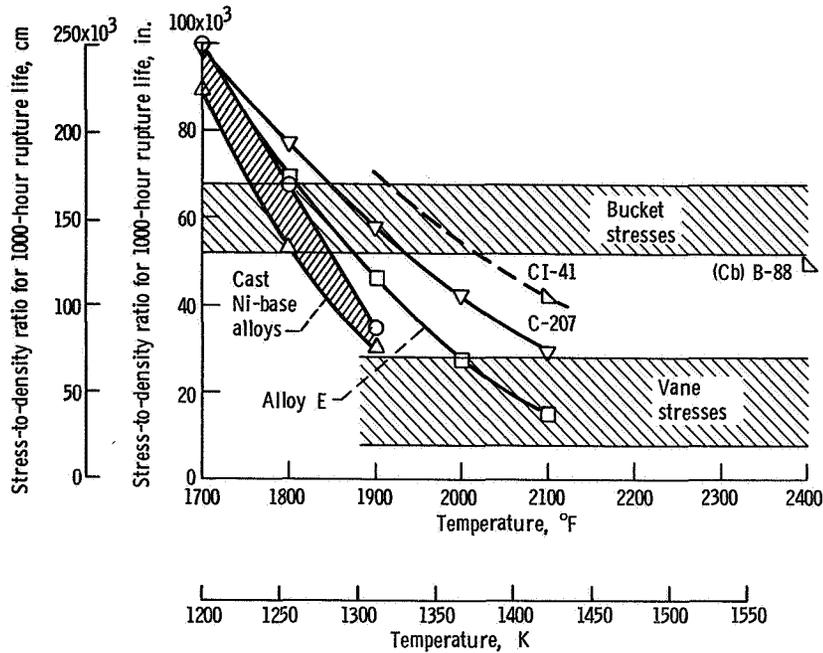Figure 12. - Trade-off between strength and ductility of chromium alloys.

Figure 13. - Rupture strength of nickel, chromium, and columbium alloys.

The extrapolated long-time strengths of current chromium alloys are compared with those of nickel and columbium alloys on a density-compensated basis in figure 13. In the stress range of interest for turbine buckets, alloy E offers a 25° F (14 K) advantage over the strongest current nickel alloys, while C-207 and CI-41 offer temperature advantages of about 75° and 150° F (42 and 83 K), respectively. A columbium alloy such as B-88 would offer a temperature advantage of about 500° F (278 K), pending solution of the difficult oxidation protection problem.

Although protective coatings for chromium have been under study for several years, progress has been slow. The current status of some potential coatings for chromium is summarized in figure 14 (refs. 78 and 79). Claddings of Ni-Cr-Al have been evaluated, but are embrittling to the chromium substrate because of metallic interdiffusion. Aluminide coatings are protective from oxidation, but aluminum itself diffuses into chromium rapidly and is embrittling. In contrast, silicide coatings are not in themselves embrittling to the substrate. Although $CrSi_2$ is unable to form a protective oxide scale because of the refractoriness of Cr_2O_3, modification of the silicide with elements such as iron allows the formation of a vitreous and more protective silicate scale which substantially reduces embrittlement of the substrate. This type of coating is potentially quite attractive although the brittleness of the silicide is of some concern.
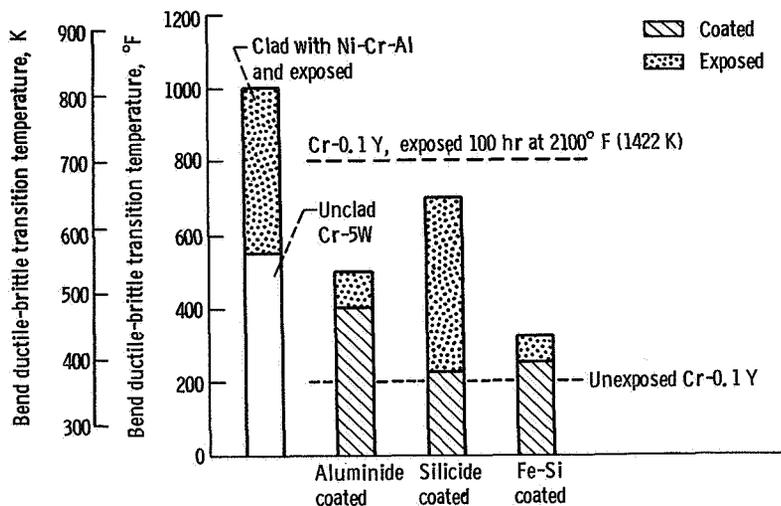
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Figure 14. - Effects of coatings on ductility of air-exposed chromium.

AREAS FOR FUTURE WORK

It is possible at this time to identify the most critical problems associated with the development of useful chromium alloys and to suggest some profitable avenues for future work.

The most critical current problems in the development of chromium are, in order of importance: (1) the protection of chromium from oxidation/nitridation-embrittlement; (2) improvement in the intrinsic impact ductility of chromium alloys at low temperatures; and (3) further improvement in the high temperature strength of chromium.

The protection of chromium from embrittlement through nitrogen contamination during high temperature air exposure appears to require the development of a protective coating. Although alloying with yttrium and/or other rare earths improves the resistance of unalloyed chromium, the effectiveness of these additions is practically eliminated by further alloying for high temperature strength. Types of surface coatings which might prove useful include chromium compounds, particularly modified silicides, ductile claddings, and surface diffusion layers. Future work should include all three of these approaches. Silicides should be modified with elements such as iron, vanadium, molybdenum, and rhenium which form low-melting oxides and thus might be expected to help form a more vitreous silicate scale. Cladding candidates should include compatible alloys such as Cr-Y-Th-Hf which have good oxidation resistance and ductility retention. On a practical basis, it may be difficult to completely clad such a complex shape as a turbine bucket. Surface alloying to introduce protective elements at the surface through diffusion should be studied. Elements such as yttrium, thorium, and hafnium could be

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deposited by pack cementation or "metalliding" to produce an oxidation resistant surface. Any such protection method must be ultimately capable of protecting the substrate from embrittlement for times of the order of hundreds to thousands of hours in the temperature range 2000° to 2200° F.

In the evaluation of protection methods, the effects of air velocity must be considered, since it has been demonstrated that oxidation and embrittlement are different in static and high velocity air.

Improvements in the intrinsic impact ductility of chromium at low temperatures will require modifications in alloying approaches for high temperature strength. The reliance on solution strengthening should be decreased in favor of precipitate or dispersion strengthening, since solution strengthening involves a rather severe penalty in terms of increased ductile-brittle transition temperature while the latter may actually improve the low temperature ductility.

Although the strength levels achieved in current chromium alloys are competitive with advanced nickel alloys, further improvements appear possible. Specifically, further alloying studies should be directed towards precipitate-strengthened alloys. The optimum strengthening compound should be identified and the optimum amount of this compound should be determined. Stabilities with respect to solutioning and coarsening should be evaluated, and further alloying to improve the stability at fine particle sizes should be studied. Prime candidates for particle strengthening are the carbides and borides of columbium and tantalum.

Dispersion strengthening with inert particles has not been effective to date but refinement in particle sizes should be beneficial. The potential of forming fine oxide particles in situ through low pressure oxidation of a suitable binary alloy also appears to offer possibilities.

CONCLUSIONS

The following conclusions are drawn from this review of recent developments in chromium alloys:

1. The development of chromium alloys is continuing at a moderate pace. Although several attractive alloy compositions have been identified, no truly usable alloy has yet been developed. In the sense of becoming commercially acceptable, chromium alloy development is still at an early stage.

2. The major deterrent to the use of chromium alloys in jet engines and other intermediate temperature applications is embrittlement from nitrogen contamination resulting from air exposure in the 2000° F (1366 K) temperature range. Protective coatings such as those based on silicides or rare earths must be developed to eliminate this problem.

3. The ductile-brittle transition temperature of high-strength chromium alloys must be lowered as much as possible. This reduction will require a balance between solution strengthening, which tends to increase the transition temperature, and precipitate or dispersion strengthening, which tends to reduce the transition temperature.

4. The strength levels of currently available chromium alloys appear adequate for service in advanced jet engines in the 2000° to 2200° F (1366 to 1478 K) temperature range, pending a solution to the embrittlement problem. Additional strengthening should be obtainable from optimized precipitate strengthening.

Lewis Research Center,
 National Aeronautics and Space Administration,
  Cleveland, Ohio, May 12, 1969,
   129-03-06-02-22.

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