# Chromium and Chromium-Based Alloys: Problems and Possibilities for High-Temperature Service

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*This article presents an overview of publications on mechanical properties of chromium and chromium-based alloys, with particular emphasis on ductility at low temperature and strength at high temperature. Analysis of rather scattered data suggests that a chromium or chromium-based alloy can be ductilized at ambient temperature and is quite capable of being strengthened to high levels at high temperature. A new composition design and process would open new opportunities for chromium-based alloys as structural materials used at temperatures up to 1,300°C.*

## INTRODUCTION

The increased efficiency associated with higher operating temperatures in gas turbines has prompted designers to search for new materials that can be used at temperatures above the useful limit of nickel-based superalloys. Chromium metal has been considered as a possible base for alloy systems since the late 1940s due to its high melting point (1,863°C), good oxidation resistance, low density (20% less than most nickel-based superalloys), and high thermal conductivity (two to four times higher than most superalloys).[1–2] Considerable effort was made, especially from the late 1940s to the early 1970s, to explore the possibility of developing chromium-based alloys for high-temperature applications such as in jet engines.[3–6] However, this interest in chromium was short-lived. Two major disadvantages held back its commercial exploitation. First, chromium has a high ductile-to-brittle transition temperature (DBTT),[1] which is commonly above room temperature in tension and is a characteristic shared with its sister elements, molybdenum and tungsten. Second, chromium exhibits further embrittlement resulting from nitrogen contamination during high-temperature air exposure. Since the late 1970s, chromium, as a practical alloy base, has remained virtually unstudied.

Recently, a new look has been taken at chromium-based alloy systems.[7–12] This article will show that chromium, providing some of its disadvantages could be eliminated or minimized, actually has a rather attractive potential as an alloy system base. Some research efforts directed toward improvement of the mechanical properties of chromium and chromium alloys will be reviewed in this article. Among the major points emphasized here will be the importance of considerations in controlling of ambient ductility and of precipitate strengthening at high temperatures.

## DUCTILITY AT AMBIENT TEMPERATURE

One of the major disadvantages of chromium is its almost complete lack of ductility below the DBTT, which for unalloyed recrystallized chromium with commercial purity is approximately 150°C.[13] Some researchers believed this brittleness is intrinsic to chromium, which shows a sharp transition over a small range of temperatures from ductility to brittleness.[14] However, because the chromium with electrolytic high purity exhibits adequate tensile and bend ductility at room temperature,[14,15] chromium is certainly not inherently brittle at room temperature. Some external causes may influence the DBTT and ductility at room temperature.

## MAIN INFLUENCE FACTORS

### Impurities

The presence of a DBTT in chromium is associated with impurities because the DBTT is lowered as purity increases. The main impurities studied are nitrogen, carbon, oxygen, sulfur, and hydrogen.[16–19] For chromium in as-cast and slowly cooled heat-treated condition, nitrogen content in the range of 0.005–0.03 ppm has relatively little effect on the DBTT and, thus, the ductility of the chromium.[16] However, as the nitrogen content is increased, the DBTT of chromium (as-cast, cold-worked, or recrystallized) rises rather sharply.[20,21] Therefore, the heat-treatment process, including annealing temperature and cooling rate, has a great effect on the DBTT. Normally, the DBTT increases with increasing cooling rate because of the retention of appreciable amounts of nitrogen in supersaturated solid solution.

However, not all investigators agreed that nitrogen is detrimental to the ductility of chromium and pointed out that nitrogen in solid solution has little effect on the DBTT and that the embrittling effect of quenching is attributable to a decrease in the size of the nitride precipitate through increased coherency strains between the precipitate and the chromium matrix.[22,23] Subsequent work[24,25] showed that it is very difficult to retain significant amounts of nitrogen in solid solution by quenching and only 6 ppm nitrogen is retained in solution at room temperature after cooling at a rate of 40°C per second and 25 ppm at 900°C per second.

In conclusion, it is apparent that the embrittling effects of nitrogen are a complex function of composition, thermal history, mechanical treatment, specimen preparation, and testing procedures. The embrittling mechanisms of nitrogen are not completely clear.

The DBTT of cast chromium increases as carbon content increases while the fracture of the alloys becomes more and more intergranular.[16] The harmful effect of carbon appears to be due to the formation of brittle carbides in the grain boundaries.

Oxygen is the most prevalent impurity in high-purity chromium, but there is little evidence that it influences ductility to any important extent. Oxygen up to 0.34% has no appreciable effect on the DBTT of cast chromium.[16] A minor increase in transition temperature in bending for recrystallized chromium sheet resulted when the oxygen was raised from 0.05% to 0.18%, though there was no measurable increase for as-rolled sheet.[26] Small amounts of sulfur (0.02%) make chromium impossible to warm roll.[26] An alloy containing 4.5% sulfur was brittle at temperatures as high as 500°C, and fracture occurred along sulfide phases at the grain boundaries.[16]

Hydrogen is present in large amounts in as-deposited electrolytic chromium but is evolved on heating above 400°C.[13,27] It is commonly removed by degassing in vacuum at 700–900°C. No data is available for the effect of hydrogen on the DBTT.

### Surface Condition

Chromium is extremely notch-sensitive.[28] Swaged chromium rods are brittle as produced but, after removal of the surface layer, could be reverse-bent repeatedly at room temperature without fracture and have tensile elongations up to 26%.[29] The specimens with mechanically prepared surfaces can still be ductile provided that the material is of sufficiently high purity. The surface condition and various heat treatments on the DBTT of swaged chromium rods has also been observed by Wain et al., and their results support that chromium is notch sensitive.[14,20] However, it is not clear from all this work whether the effects noted arise from micro-notches in the surfaces or from the presence of a very heavily cold-worked layer.

### Structure

It is generally known that recrystallization raises the DBTT of wrought high-purity chromium (i.e., chromium can tolerate more impurities [nitrogen] in the cold-worked than in the recrystallized condition).[30,31]

The grain size of unalloyed chromium has an influence on the DBTT: fine-grained samples displayed the DBTT at 90°C, coarse and mixed structures at about 30°C, and single crystals between –78°C and –196°C.[30] These results suggest that structure, especially the structure of the grain boundary, may play an important role in the brittle behavior of chromium. See the sidebar for details on brittleness mechanisms.

## IMPROVING DUCTILITY

### Purification

Because the DBTT is lowered as purity increases, purification is an obvious way to decrease the DBTT and thus increase the ductility at low temperature.[16–18] According to theoretical and experimental observations, removal of nitrogen (and possibly other similar elements) to extremely low levels, certainly <0.0001%, should result in adequate ductility in all conditions. Such purification is possible in principle, but it is doubtful whether it can be achieved and maintained in practice. Meanwhile, research proves that suitable ductility can be found in chromium or chromium alloys of lesser purity.[11] But their purities are still high and the maintenance of this purity during fabrication and service is relatively expensive.

### Alloying

Another obvious expedient for effectively improving the ductility at low temperature is either to stabilize or to remove the interstitial impurities such as nitrogen, carbon, and oxygen or sulfur that may be present in chromium by adding a scavenging element. An alloying addition may also decrease the DBTT and thus raise the ductility of chromium alloys.

The earliest work of this type was

## BRITTLENESS MECHANISMS

Several theories have been used to explain the low-temperature brittleness or the high ductile-to-brittle transition temperature of chromium.

The brittleness is suggested to be an irrevocable consequence of the change in electronic structure occurring at the Neel temperature.[32] However, this theory can be discounted since it seems to have arisen out of a correlation between the onset of brittleness and an erroneous Neel temperature, and also since chromium can behave in a ductile manner at temperatures well below the Neel temperature currently accepted.

The brittle fracture in chromium has also been proposed to be a strain-induced precipitation mechanism involving a chromium nitride precipitation.[33] But strain-induced precipitation, which may take place at the higher temperatures characteristic of brittle fracture in less-pure chromium, would not be expected to occur at temperatures of 100°C or less. Meanwhile, this mechanism could not explain why brittleness can be produced by very small amounts of nitrogen in solid solution.

The ductility of chromium may also be controlled by the amount and orientation of grain-boundary impurities[27] because wrought chromium possessing a fibered grain structure is ductile in tension at room temperature while a recrystallized grain structure is completely brittle.

A Cottrell dislocation locking mechanism due to the solute nitrogen has been suggested.[20] It was theorized that nitrogen could form a Cottrell atmosphere in chromium, which could be followed, under certain circumstance, by precipitation in dislocation lines. The chromium in which the dislocations are anchored by nitrogen atoms could lead to brittle fracture, as postulated by the Mott-Stroh theory. However, the work[34] of Hook and Adair indicated that chromium's brittleness cannot be eliminated even if pre-straining 2% and 8% to produce large numbers of free dislocation does enhance ductility to some extent. Moreover, ageing to re-lock the dislocation after pre-straining does not embrittle chromium provided the ageing treatment is carried out below the recrystallization temperature.[35]

Several observations suggest that brittle fracture in chromium is slip-induced and the critical stage of fracture is crack initiation.[31,36,37] Further, in polycrystalline chromium tested in tension, evidence points to the conclusion that the initial crack formed is a result of slip-induced grain boundary parting which initiates trans-granularly and subsequently propagates mainly by cleavage. The brittle vs. ductile fracture of chromium, then, appears to be a competition between slip-induced crack initiation and macroscopic flow. If the specimen can pass through the initial stage of yielding without cracking, then deformation can proceed, permitting a high elongation before cleavage fracture occurs.[38]

Therefore, the whole picture of chromium brittleness is something of an unresolved issue.

carried out by Sully and his co-workers in the early 1950s.[1] Eyan[39] and other researchers[16,40,41] investigated the elements (Ce, La, Hf, Th, Ti, U, Y, Zr) that readily react with nitrogen in chromium during melting and casting, and found that Ce, Ti, Y, and Zr additions promote room-temperature ductility in recrystallized chromium. Niobium and tantalum have also been shown to improve the ductility of fabricated and annealed chromium, but erratic results were reported.[42] Silicon is a relatively sluggish and probably weak nitride-former and aluminum results in a small but definite improvement of the ductility of chromium.[15,26,43,44] Boron addition can modify the nitride impurity after heat treatment and reduce the DBTT of impure cast chromium.[45]

Some researchers attempted to correlate properties of the alloying element with its effect on the DBTT and their work indicated that the effect of alloying on the DBTT of chromium is not directly related to the atomic size of the solute atoms.[46] However, Carlson et al. indicated that the DBTT of chromium-based alloys is dependent primarily on the atomic size of the alloying elements and concluded that the DBTT of iodide chromium is decreased by the addition of solute atoms that form solid-solution alloys and have atomic diameters larger than chromium but not exceeding the 15% size limit.[40] They also suggested that elements with atomic diameters between 2% and 10% larger produce the maximum decrease in the DBTT and alloying additions that exhibit little or no solid solubility in chromium and have atomic diameters that exceed the 15% limit all raise the DBTT of high-purity chromium. Additions of metals that form carbides, nitrides, and oxides that are more stable than the corresponding chromium compounds increase the DBTT rather sharply, which is the converse of what has previously been observed on chromium of lesser purity.

## Rhenium Ductilizing

Alloying a relatively high rhenium (at least 20 at.%) to chromium can considerably improve its fabricability and low-temperature ductility.[47] Several observations[48,49] have been done to investigate the ductility and strength properties of chromium alloyed with rhenium additions ranging from zero up to 40 at.% and numerous suggestions have been put forward to explain the mechanisms by which rhenium effects this remarkable improvement in the cold ductility of chromium.[50] However, the validity of these suggestions remains unsubstantiated.

Several non-rhenium systems appear to be rhenium analogs, exhibiting the improved ductility and twinning associated with the rhenium-ductilizing effect. Improved low-temperature ductility in concentrated and single-phase Cr-Ru alloys has been observed.[51] Chill-cast Cr-50Fe[52] and Cr-35Co alloys,[47] Cr-10Ir, Cr-55Mn, and Cr-65Mn were also found to exhibit fair fabricability[47] while alloys of Cr-Ti, Cr-V, Cr-Mo, and Cr-Ta were unfabricable.[53]

From these observations, Klopp[48] suggested several common characteristics of solutes promoting the rhenium-ductilizing effect:

- The ductilizing solutes are from Groups VIIa and VIIIa of the periodic table
- The ductilizing solutes form intermediate sigma phases with chromium
- The ductilizing solutes have relatively high solubilities in chromium, at least 20 at.%
- Maximum cold ductility occurs in saturated or supersaturated single-phase solid-solution alloys

## Solution Softening

In addition to the rhenium-ductilizing effect, the cold ductility of chromium can be improved by alloying to promote solution softening. Solution softening is an initial drop in hardness at low concentrations followed by an increase caused by solid-solution hardening, and is first observed in dilute W-Re and Mo-Re alloys.[53] It was later determined that the decreased hardness of these alloys was accompanied by reductions in the DBTT. Stephens et al.[50] found that alloy softening existed in the Cr-Re system, occurring at homologous temperatures less then 0.16 Tm and at the rhenium concentrations less than 16 at.%. Allen et al.[54] investigated the room-temperature hardness of iodide chromium containing binary additions of Group IVa to VIII metals (Ti, Zr, Hf, V, Nb, Ta, Mo, W, Mn, Re, Fe, Ni, Co, Ru, Pd, Os, Ir, and Pt) up to 65 at.% and found that each alloy series, as arc-cast or homogenized, shows a hardness minimum as a function of alloy concentration near 0.5 at.%. However, as indicated previously, adding some of these elements, like hafnium and zirconium, to chromium does not decrease the DBTT. Therefore, the relationship between alloy softening and the DBTT in chromium needs more investigation. As to the mechanism that produces alloy softening, there is not a certain explanation and the following two have received most consideration: lowering the Peierls stress, which is assumed to be high for body-centered cubic metals,[55] and scavenging of interstitial impurities.[56]

## Pre-Straining

The DBTT of chromium can be reduced by first pre-straining chromium alloys above the DBTT to produce mobile dislocation. The pre-straining can be done conventionally[34,57] or by hydrostatic pressurization.[58] Once mobile dislocations are available, multiplication can occur and macroscopic flow will proceed until the material is sufficiently work-hardened that ductile cleavage fracture stress is reached.

## Second-Phase Particles

Solie's[59] observation indicates that nitride particles in chromium can act as crack nucleation sites once they have reached a critical size and that the DBTT is dependent upon the size and concentration of these particles. Thus, the alloys

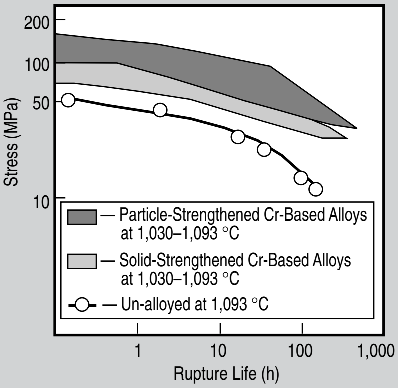

Figure 1. The stress-rupture properties of chromium-base alloys.

that contain a second phase, either intergranularly or along the grain boundary, might be expected to have a higher DBTT due to the presence of additional crack nucleation sites.

However, several studies demonstrated that certain oxides,[38] borides,[54] carbides,[60–62] and nitrides[25] of Group IVa and Group Va elements, when produced by reaction in the melt in the solid state or by internal nitridation, lower the DBTT of recrystallized chromium in tension (~300°C) to room temperature or below, particularly when a rare-earth element has also been added. The basic premise is that particles would disperse slip, thus reducing the dislocation pile-up length at sites for crack nucleation (e.g., grain boundaries). This would raise the macroscopic cleavage and the DBTT would be shifted to lower temperatures. The results of Wilcox et al.[38] in the Cr-ThO$_2$ alloy and Ryan et al. in the Cr-TaC alloy support this premise.[62]

### Processes

Because grain-boundary ruptures are frequently the origin of brittle failure in polycrystalline chromium, and because coarse-grained samples are more ductile than fine-grained, directionally solidified and single-crystalline technologies may be the most suitable ways to get ductile chromium alloys.[31]

## HIGH-TEMPERATURE DUCTILITY

An even more serious problem of chromium-based alloys is the further severe embrittlement that results from nitrogen contamination during high-temperature air exposure. Chromium alloys are not subject to catastrophic oxidation but they do not have adequate oxidation resistance for use unprotected in an air environment above 1,100°C. Attempts to overcome the problem of nitridation embrittlement have included alloying with nitride-forming elements,[63] the use of surface-protective coating or clad,[64] and the incorporation of dispersed oxide phases in the chromium matrix.[65]

The utility of claddings to protect a chromium alloy from oxidation and nitrogen absorption during cyclic exposure in air at 1,150°C and 1,260°C was examined by Williams and coworkers.[66] Their results indicate that a barrier layer of aluminized nickel base can prevent inter-diffusion between the cladding alloy and the chromium alloy. Such a barrier can protect chromium alloys from nitrogen absorption and oxidation at 1,150°C, but not at 1,260°C.

The use of yttrium as a scavenger has been found to greatly improve the ductility and the resistance to oxidation/nitrogen embrittlement in chromium systems.[67] A complex of Cr + Y + La coating has been suggested and would offer the most potential for protecting chromium alloys from nitrogen embrittlement. The effect of a ruthenium addition on the ductility and oxidation behavior of chromium was investigated by Wukusick[51] and Tedmon,[68] and their results showed that the higher ruthenium alloy oxidized at slower rates than did pure chromium.

Lawn's investigation indicated that the pure chromium suffered nitridation in the form of extensive internal precipitation of chromium nitride needles after 100 h at 1,200°C and the yttria-dispersed chromium was essentially free from this effect.[69] Dispersed spinel phases, such as MgO•Cr$_2$O$_3$ and MgO•Al$_2$O$_3$, may take up nitrogen from a chromium matrix at nitrogen levels far in excess of those normally required to form chromium nitride precipitates in the pure (oxide free) metal. A similar effect has also been identified in chromium alloyed with yttria-dispersed chromium alloys (Cr-2Y$_2$O$_3$ and Cr-5Y$_2$O$_3$).[65] However, the effectiveness of yttrium and yttrium oxide dispersion is lost at 1,250°C or above,[65,70] where volatilization of the chromic scale is likely to play an important role in the oxidation process. Thus, the problem of nitrogen embrittlement does not appear amenable to solution by alloying, such as with yttrium or ruthenium. Surface protection is therefore considered essential for useful service life at elevated temperatures. Protective coatings, claddings, or special surface-alloying techniques must be developed if chromium alloys are to be useful at high temperatures in air.

## HIGH-TEMPERATURE STRENGTH

Unalloyed chromium has low strength, about 200 MPa at room temperature and 70 MPa at 1,200°C under compression tests.[4,5] Strengthening by alloying addition is a widely employed approach for many metals. Early alloy development studies on chromium also tended to emphasize solution strengthening. Up to a sevenfold increase in the high-temperature strength of chromium can be achieved by the addition of solid-solution hardening elements such as rhenium, tungsten, and molybdenum. Unfortunately, most solution-strengthening solutes significantly increase the DBTT and have a deleterious effect on the low-temperature ductility of chromium.[40,71] Exceptions are Fe, Co, Re, and Ru, which at large alloying concentrations promote ductility through the "rhenium-ductilizing effect." But this alloying increases the density of the alloys greatly.

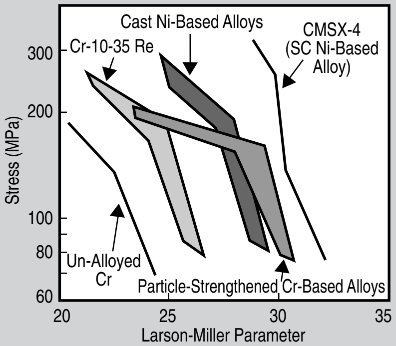

Figure 2. A summary of creep-rupture properties of some chromium-base alloys compared with some nickel-base alloys.

Since solid-solution strengthening raises the DBTT or the density in chromium-based alloys, it appears that effective use of precipitation hardening or dispersion strengthening is a promising way to develop chromium-based alloys with a more usable combination of low-temperature ductility and high-temperature strength. According to the available data, greater improvement can be achieved by precipitation strengthening, with less serious effect upon the DBTT.[72,73] Oxides,[65,74] because of their high free energy of formation, are generally recognized as ideal dispersions. On the other hand, certain borides,[75] carbides,[76] and nitrides,[23,77] although less stable than oxides, are attractive since they can be incorporated as strengthening dispersions by conventional alloying and fabrication practices.

## CREEP AND RUPTURE

In the development of alloys for use as vanes or blades in gas-turbine engines, good creep strength at high temperatures is a major requirement. However, pure chromium has very low creep resistance. For re-crystallized swaged chromium, the stress for the stress-rupture fracture in 10 h is about 122 MPa at 760°C and below 15 MPa at 1,214°C.[77]

By using solid-solution hardening of molybdenum and tungsten, the tensile creep strength of extruded chromium at 950°C can be substantially improved.[78] The time to fracture for a Cr-5Mo alloy at 950°C under stress of 92 MPa is about 395 h. Alloying with tantalum or niobium is also beneficial to the creep strength and the creep life of Cr-2.0Ta is more than 120 h at 1,050°C under constant tensile load of 101 MPa.[79] But the optimum content of an alloying element such as molybdenum or tantalum in chromium is still uncertain.

For further improvement of creep resistance, particularly by precipitation hardening, a variety of chromium alloys, ranging from binary to quaternary systems with or without strengthening particulars of oxide, carbide, and boride, have been assessed by tensile or compression creep tests. Dispersion hardening by the carbides of Hf, Zr, Ta, Ti, and Nb has been demonstrated to improve the creep properties of chromium significantly.[77–81] Figure 1 shows stress-rupture curves for some dispersion-strengthened chromium alloys in the worked and recrystallized condition. Some creep-rupture results are summarized in Figure 2 and indicate that dispersion-hardened chromium alloys can only be compared with cast nickel-based alloys now. The abscissa is in the form of the Larson-Miller parameter LMP = T (C + log t), where T = absolute temperature (K), and t = time in hours. Because there are insufficient data to fix exactly the constant C, an approximate value of 20 was taken as that in nickel-based alloys.

## FUTURE WORK

Considerable progress has been made during the last five decades in understanding the brittleness of chromium and chromium-based alloys and finding ways to strengthen the materials. However, it is obvious that the DBTT is increased as the high-temperature strength increases. So the balance between high-temperature strength and low-temperature ductility must be considered according to the applications. Meanwhile, considerable improvements are still required to obtain strength levels of sufficient magnitude to interest engine manufacturers in chromium-based materials to replace the current nickel-based alloys.

Recently, the search for alloys capable of extended use at a service temperature in excess of nickel-based alloys, 1,100°C, has revived interest in chromium-based alloys. Recent research has demonstrated that the tensile ductility of commercialy pure chromium (99.8 at.%) can be dramatically improved by alloying with trace silver. A Cr-Ag alloy was subjected to about 20% tensile elongation at ambient temperature, which creates a definite possibility to produce the ductile chromium-based alloys for use at high temperatures.[82] Ro et al.[12] found that alloying with rhenium and tungsten can make a chromium-based alloy with enough compression ductility at room temperature and superior high-temperature strength compared with existing nickel-based superalloys at 1,200°C. Liu et al.[7–10,83–85] suggested that the intermetallic $Cr_2X$ (X = Zr, Hf, Nb, or Ta) is more attractive than the carbide to strengthen chromium-based alloys since the available information indicates that it could form during ageing at a temperature near the service temperature. The substantial progress in the development of high-temperature coating design and types makes it possible to protect chromium from oxidation/nitrogen embrittlement during high-temperature air exposure up to 1,300°C.[86,87] All the research indicates new ways to develop new chromium-based alloys with good potential as structural materials in applications at temperatures even up to 1,300°C.

The most critical current problems in the development of chromium-based alloys are, in order of decreasing importance:

- Further improvement in high-temperature strength
- The protection of chromium-based alloys from oxidation/nitridation embrittlement
- Improvement in the impact ductility at ambient temperature

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