Wrought Cobalt-Base Superalloys

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Wrought cobalt-base superalloys are used extensively in gas turbine engines because of their excellent high-temperature creep and fatigue strengths and resistance to hot corrosion attack. In addition, the unique character of the oxide scales that form on some of the alloys provides outstanding resistance to high-temperature sliding wear. This article provides a review of the evolutionary development of wrought cobalt-base alloys in terms of alloy design and physical metallurgy. The topics include solid-solution strengthening, carbide precipitation characteristics, and attempts to introduce age hardening. The use of PHACOMP to enhance thermal stability characteristics and the incorporation of rare-earth elements to improve oxidation resistance is also reviewed and discussed. The further development of cobalt-base superalloys has been severely hampered by past political events, which have accentuated the strategic vulnerability of cobalt as a base or as an alloying element. Consequently, alternative alloys have been developed that use little or no cobalt. One such alternative, Haynes® 230™ alloy, is discussed briefly.

1. Introduction

WHEN one examines the history of aero-engine development, cobalt-base alloys emerge as the first true members of the superalloy family. An historical perspective of these materials is given in Table 1. The initial applications involved cast compositions for use as blades in turbosuperchargers for piston engines in the 1930s, then as blades and vanes in the first gas turbine engines of the 1940s. The use of cast cobalt-base alloys survives in current gas turbine engines mainly as nozzle guide vanes and stator blades. Wrought cobalt-base alloys did not enjoy extensive usage until the 1950s for such components as forged turbine blades, combustor liners, and afterburner tailpipes. However, their development and use were greatly overshadowed by the advent of nickel-base superalloys. Currently, only a handful of wrought cobalt-base superalloys enjoy any usage of commercial significance. However, their attractive high-temperature creep and fatigue strengths, resistance to hot corrosion, and wear resistance provide them special niches in a variety of component applications, which should ensure their continued use for many years.

2. Alloy Composition and Physical Metallurgy

The compositions of some important wrought alloys are given in Table 2. The roles of the various alloying elements are summarized in Table 3.[1] Cobalt provides a unique alloy base because of its allotropic fcc to cph phase transformation, which occurs at a temperature of approximately 422 °C (792 °F).[2] Alloying elements such as iron, manganese, nickel, and carbon tend to stabilize the fcc structure and increase stacking fault energy, whereas elements such as chromium, molybdenum, tungsten, and silicon tend to stabilize the cph structure and decrease stacking fault energy.[3] The fcc to cph transformation reaction

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is quite sluggish even for pure cobalt. However, in metastable compositions, it can be promoted by cold work via a mechanism involving the coalescence of stacking faults.[4] This phenomenon provides a practical limit in the design of wrought cobalt-base alloys in terms of the manufacturing methods that can be used to produce various product forms. Those involving hot working operations such as plate, bar, and hot rolled sheet do not present obstacles, because the working temperatures typically are well within the stable fcc range. However, those products that require extensive cold working sessions, such as cold rolled sheet, cold drawn tubulars, and cold drawn bar and wire products, must possess adequate levels of matrix stability to be economically viable. Such stability usually is imparted through additions of nickel.

For imparting resistance to oxidizing and sulfidizing types of environments, chromium is the preferred alloying element. Attempts to incorporate aluminum in amounts sufficient to provide protective alumina scales have not been commercially successful, because the formation of the brittle intermetallic compound β-CoAl significantly reduced fabricability. In addition to chromium, small amounts of elements such as manganese, silicon, and rare-earth elements (e.g., lanthanum) can be used to enhance the formation of protective oxide scales at elevated temperatures.

The high-temperature strengthening of wrought cobalt-base alloys is accomplished mainly through the use of solid-solution

Table 1   Cobalt-base superalloys: historical perspective

Co-Cr alloys first patented by Elwood Haynes	1907
Haynes® alloy 6B	1913
Stellite® alloy 21 (Vitallium® supercharger buckets)	1936-1943
Stellite® alloy 31 (X-40) buckets	1941-1943
S816 alloy wrought buckets	1946-1953
Haynes alloy 25 afterburner components	1948-1955
MAR-M® 302 vanes	1958
Airesist® vanes	1964
Haynes alloy 188 combustor, afterburner components	1966-1968

Note: Haynes is a registered trademark of Haynes International, Inc.; Stellite is a registered trademark of Thermadyne, Inc.; MAR-M is a registered trademark of Martin Marietta Corp.; Airesist is a registered trademark of Allied Signal Aerospace Co.; and Vitallium is a registered trademark of Pfizer Hospital Products Group, Inc.

Table 2 Compositions of wrought cobalt-base superalloys

Alloy	Ni	Fe	Cr	Mo	Composition, wt% W	C	Mn	Si	Ti	Others	Co
Haynes alloy 6B	2.5	3(a)	30	1.5(a)	4	1.0	1.4	0.7	...	...	Bal
Haynes alloy 25	10	3(a)	20	...	15	0.10	1.5	0.4(a)	...	...	Bal
Haynes alloy 31	10.5	2(a)	25.5	...	7.5	0.50	1(a)	1(a)	...	...	Bal
Haynes alloy 150	...	21	28	...	...	0.05(a)	1(a)	1(a)	...	...	Bal
Haynes alloy 188	22	3(a)	22	...	14	0.10	1.25(a)	0.35	...	0.03 La	Bal
MP35N® alloy	35	...	20	10	...	...	...	...	...	...	Bal
MP159® alloy	25.5	9	19	7	...	...	...	...	3	0.6 Nb, 0.2 Al	Bal

Note: MP35N and MP159 are registered trademarks of SPS Technologies, Inc. (a) Maximum.

Table 3 Role of various alloying elements in cobalt-base superalloys

Element	Effect
Chromium	Improves oxidation and hot corrosion resistance; produces strengthening by formation of M_7C_3 and $M_{23}C_6$ carbides
Nickel	Stabilizes fcc form of matrix; produces strengthening by formation of intermetallic compound Ni_3Ti; improves forgeability
Molybdenum, tungsten...	Solid-solution strengtheners; produces strengthening by formation of intermetallic compound Co_3M; formation of M_6C carbide
Tantalum, niobium	Solid-solution strengtheners; produces strengthening by formation of intermetallic compound Co_3M and MC carbide; formation of M_6C carbide
Carbon	Produces strengthening by formation of carbides MC, M_7C_3, $M_{23}C_6$, and possibly M_6C
Aluminum	Improves oxidation resistance; formation of intermetallic compound CoAl
Titanium	Produces strengthening by formation of MC carbide and intermetallic compound Co_3Ti with sufficient nickel produces strengthening by formation of intermetallic compound Ni_3Ti
Boron, zirconium	Produces strengthening by effect on grain boundaries and by precipitate formation; zirconium produces strengthening by formation of MC carbides
Yttrium, lanthanum	Increase oxidation resistance

Fig. 1 Carbide precipitation on dislocations observed for a specimen of Haynes alloy 188 creep tested at 927 °C and 41.4 MPa (1700 °F and 6 ksi).

alloying elements such as molybdenum, tungsten, tantalum, and niobium in combination with carbon to promote carbide precipitation. The solid-solution alloying elements tend to lower the stacking fault energy, thereby, making the cross-slip and climb of glide dislocations more difficult. In addition, the diffusion of substitutional alloying elements tends to be slower in cobalt than in nickel,[5] which gives the cobalt base an inherent advantage in high-temperature creep. Carbide precipitation, especially $M_{23}C_6$ carbides, is another important key to the strengthening of cobalt-base alloys. Such precipitation can be quite effective in pinning glide dislocations, as illustrated in Fig. 1. However, the use of high levels of carbon will limit manufacturing operations to hot working processes. Compositions intended for cold working processes usually contain carbon at levels of 0.15% or less. For service temperatures of 704 °C (1300 °F) or less, special alloy compositions have been
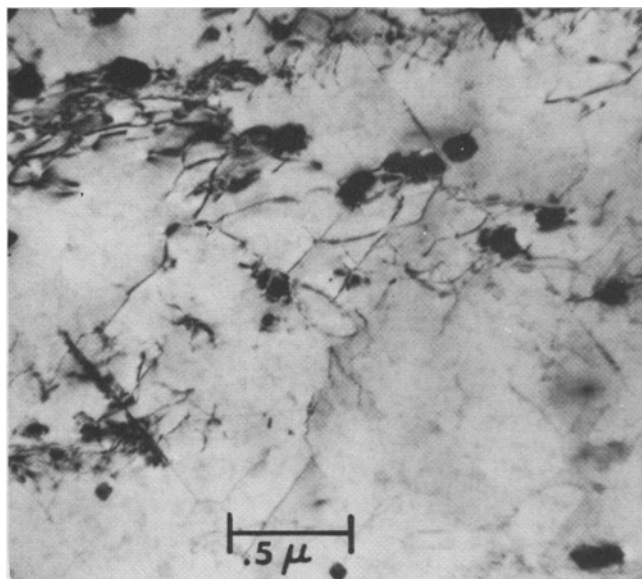
developed that exploit the fcc to cph transformation in products that are mechanically worked and aged.[6] Attempts have been made to develop age-hardenable alloys based on Co_3Ti- and Co_3Ta-type precipitates. However, problems with the thermal stability of the precipitates and the fact that the strength levels attained were easily matched or exceeded by the γ'-strengthened nickel-base alloys precluded their commercial introduction.[1]

Another important aspect in the physical metallurgy of cobalt-base alloys is the occurrence of deleterious intermetallic compounds such as the σ, μ, and Laves phases. The first two are classified as electron compounds, and they are often referred to as topologically closed-packed (tcp) phases. The Laves phase is formed mainly on the basis of atomic size factors. Some examples of these compounds in terms of general composition and crystal structure are given in Table 4. Specific data for Haynes® alloy 25 is listed in Table 5.[7] In addition to the gross chemistry factors responsible for the formation of these compounds, it has also been recognized that minor elements, notably silicon, can play important roles.[8,9] The precipitation of
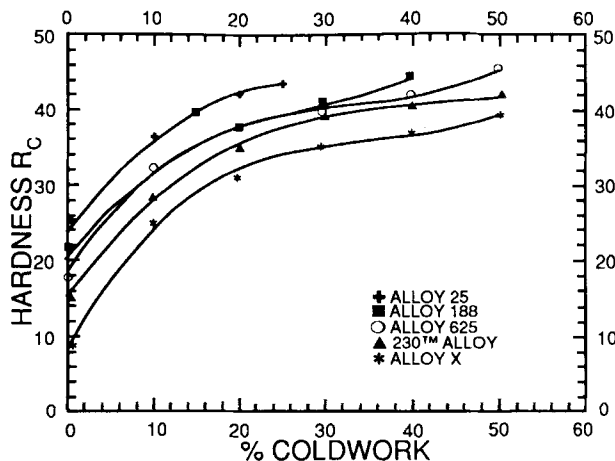
Fig. 2 Hardness versus cold work for cold reduced sheet of various alloys.

Table 4 Deleterious intermetallic compounds in cobalt-base superalloys

Compound	Structure
Co$_2$(Mo, W, Ta, Nb)	Hexagonal Laves phase
Co$_2$(Mo, W)$_6$	Rhombohedral, hexagonal μ phase
Co$_2$(Ta, Nb, Ti)	Cubic Laves phase
Co$_2$(Mo, W)$_3$	σ phase

Table 5 Phases present in Haynes alloy 25

Phase	Crystal structure	Lattice parameters, Å
M$_7$C$_3$	Hexagonal (trigonal)	$a = 13.98, c = 0.53, c/a = 0.324$
M$_{23}$C$_6$	fcc	$a = 10.55$ to 10.68
M$_6$C	fcc	$a = 10.99$ to 11.02
Co$_2$W	Hexagonal	$a = 4.730, c = 7.700, c/a = 1.628$
α-Co$_3$W	Ordered fcc	$a = 3.569$
β-Co$_3$W	Ordered hexagonal	$a = 5.569, c = 4.10, c/a = 0.802$
Co$_7$W$_6$	Hexagonal (rhombohedral)	$a = 4.73, c = 25.5, c/a = 5.39$
Matrix	fcc	$a = 3.569$
Matrix	cph	$a = 2.524, c = 4.099, c/a = 1.624$

these intermetallic phases can cause embrittlement, especially at low temperatures. Some success in retarding the formation of the Laves phase was achieved in the development of Haynes[®] alloy 188 through Nv[10] control of the chemistry using the PHACOMP[10] approach.[11]

3. Mechanical Properties

3.1 *Work Hardening Characteristics*

Cobalt-base alloys exhibit rapid hardening with respect to cold work when their composition is not fully stabilized relative to the fcc to cph transformation. This behavior is illustrated for alloy 25 (10% Ni) in Fig. 2, which includes data for several nickel-base alloys for comparison. In contrast, the hardening characteristics of alloy 188 (22% Ni), which is fully stabilized,
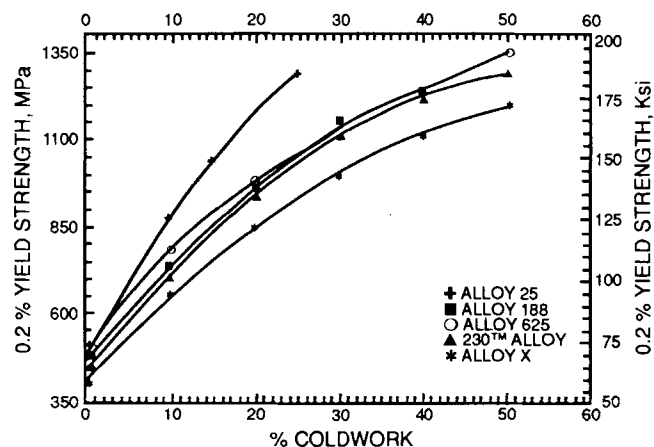

Fig. 3 Room-temperature 0.2% yield strength versus percent cold work for various solid-solution strengthened alloys.
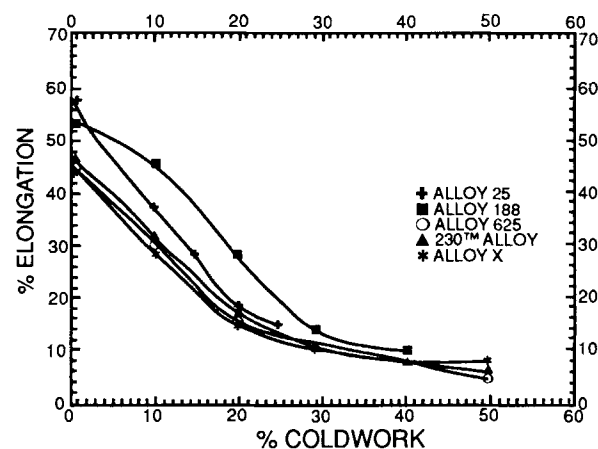

Fig. 4 Room-temperature tensile elongation versus percent cold work for various solid-solution strengthened alloys.

are very similar to those for alloy 625. As one would expect, the hardening responses are reflected in the corresponding yield strength values obtained, as shown in Fig. 3. Surprisingly, however, the residual levels of ductility observed for the cobalt-base alloys tended to be higher than those of the nickel-base alloys, as illustrated in Fig. 4. These data clearly indicate that metastable cobalt-base compositions require higher levels of force during forming operation. Stable compositions, on the other hand, should have forming characteristics similar to the nickel-base alloys.

3.2 *Yield Strength and Stress-Rupture Properties*

Within the class of solid-solution strengthened alloys, the cobalt-base alloys tend to have relatively high yield strength properties over a broad temperature range, as illustrated in Fig. 5. These strengths are easily surpassed by a γ' strengthened alloy such as alloy R-41, but for many applications requiring ease of fabrication, especially weldability, the solid-solution strengthened alloys are greatly preferred. A similar situation exists in terms of high-temperature stress-rupture strength, as
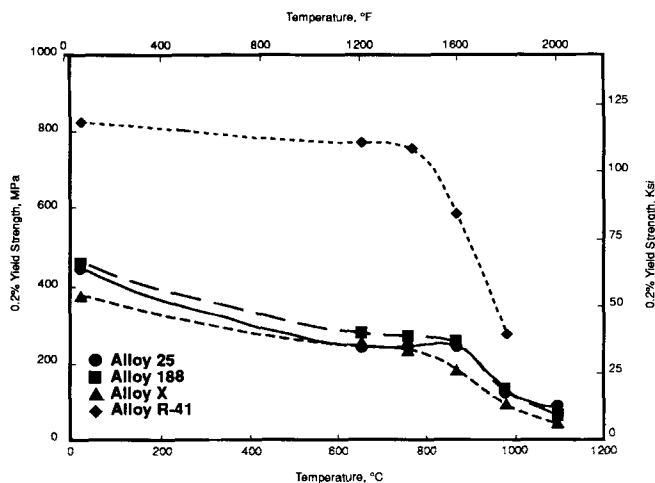
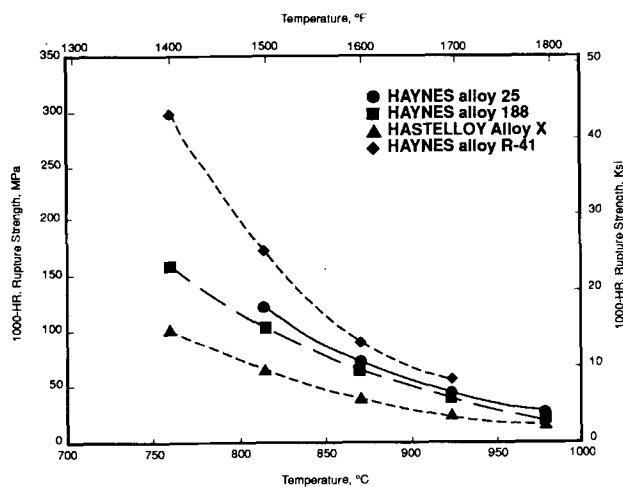**Fig. 5** 0.2% tensile yield strengths for high-temperature sheet alloys.

Fig. 7 Retained room-temperature ductility after 8000 h exposure at temperature.

Fig. 6 Comparative 1000-h stress-rupture strengths for high-temperature sheet alloys.
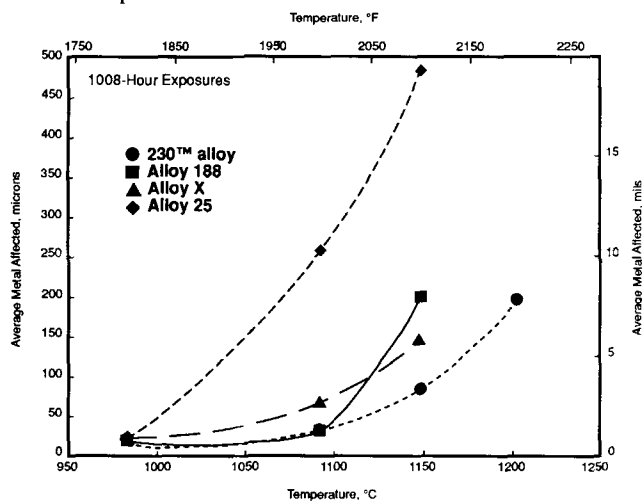
Fig. 8 Oxidation attack in flowing air for high-temperature sheet alloy.

shown in Fig. 6. When compared to a very widely used solid-solution strengthened alloy such as alloy X, the cobalt-base alloys offer a temperature advantage on the order of 55 °C (100 °F) or more.

3.3 Thermal Stability

As mentioned previously, deleterious intermetallic phases can precipitate in cobalt-base alloys, which mainly affect their low-temperature ductility properties. This behavior is illustrated in Fig. 7, which also presents comparative data for two nickel-base alloys. In the case of alloy 188, the precipitation of a Co_2W-type Laves phase was retarded through Nv control of alloy chemistry,[11] but long-term exposure in the 760 to 870 °C (1400 to 1600 °F) temperature range causes enough precipitation of the Laves phase to severely embrittle the alloy. As evident from Fig. 7, this situation is not unique to cobalt-base alloys. It has been shown for alloy X that a chromium-rich σ
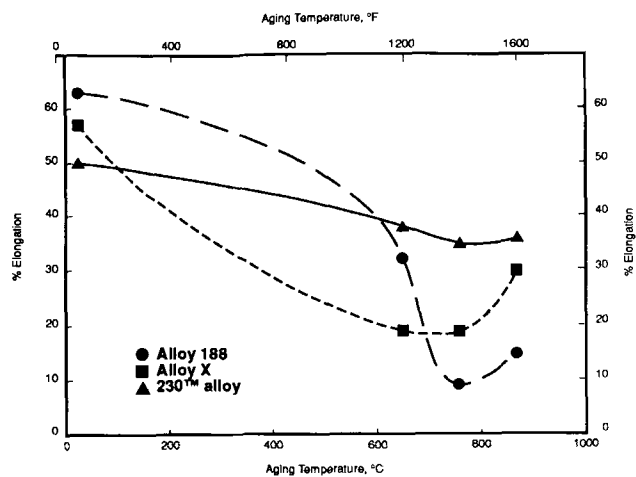
phase precipitates in the 650 to 760 °C (1200 to 1400 °F) temperature range, and a molybdenum-rich μ phase precipitates at 870 °C (1600 °F).[12] However, if the chemistry is carefully controlled to allow only normal carbide precipitation, nickel-base alloys can exhibit superior thermal stability, as illustrated for 230 alloy.[13]

4. Surface Stability

4.1 Oxidation Resistance

As a class, cobalt-base alloys are not known to be as resistant to oxidation as nickel-base alloys because of the difficulty in overcoming nonprotective CoO scales through additions of chromium.[14] This behavior is typified by the data shown for alloy 25 in Fig. 8 and 9. This problem was largely overcome in the development of alloy 188 through the use of small additions of lanthanum.[11] However, at temperatures on the order of
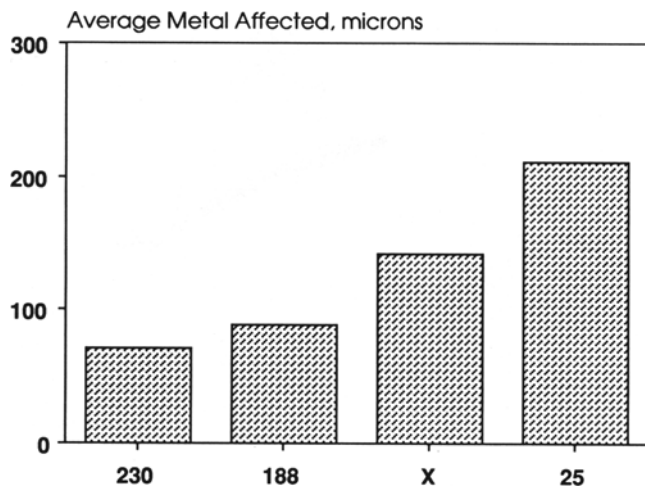
Fig. 9 982 °C (1800 °F)/1000-h dynamic oxidation data for sheet alloys.
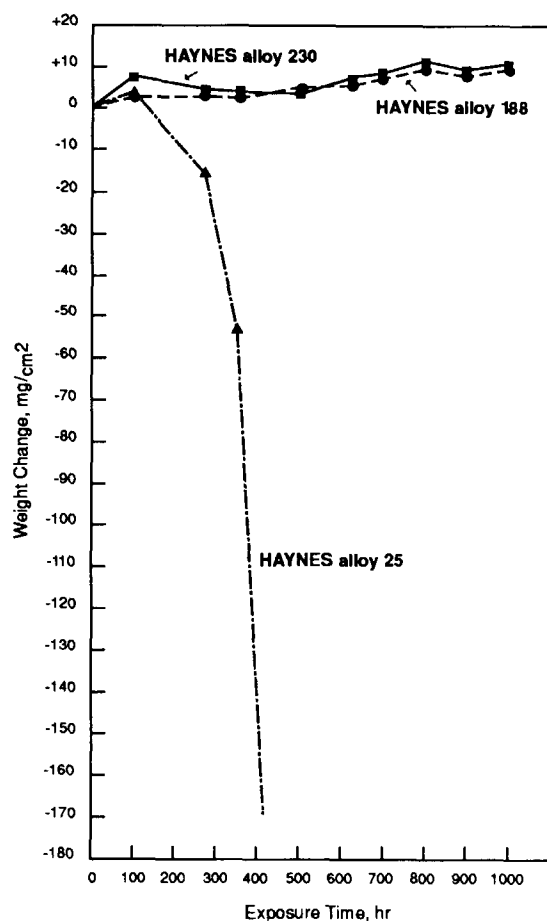

Fig. 10 Gravimetric data for Haynes alloy 230, 188, and 25 from the hot corrosion test at 900 °C (1650 °F)/50 ppm salt/0.4% sulfur fuel.

1150 °C (2100 °F) and above, the oxidation resistance of the alloy is reduced in static environments, as illustrated in Fig. 8.
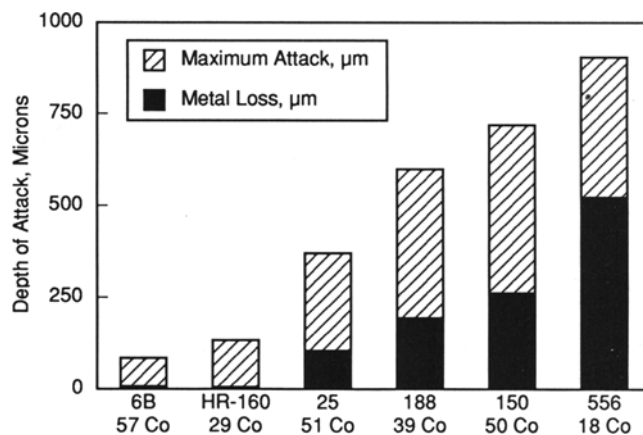

Fig. 11 Sulfidation tests at 870 °C (1600 °F)/500 h in Ar-5%H$_2$-5%CO-1%CO$_2$-0.15%H$_2$S (PO$_2$ = 3 × 10^{-19} atm, PS$_2$ = 0.9 × 10^{-6} atm).

This behavior is attributed to the formation of Co$_2$WO$_4$, which promotes low-melting point eutectics with the other oxide scale constituents.[11] Up to about 1100 °C (2012 °F), the oxidation resistance of alloy 188 is essentially equivalent to the nickel-base 230 alloy, which also contains lanthanum as a minor alloying addition.

4.2 Hot Corrosion Resistance

Hot corrosion is a complex phenomenon involving attack by oxidation and sulfidation when Na$_2$SO$_4$ deposits form on an alloy surface. The Na$_2$SO$_4$ is produced when sulfur in the fuel reacts with NaCl in the air stream as might occur in marine environments. This type of corrosion attack is particularly severe in the 870 to 950 °C (1600 to 1750 °F) temperature range. Because the melting point of the Co-Co$_4$S$_3$ eutectic, 877 °C (1610 °F), is higher than for the Ni-Ni$_3$S$_2$ eutectic, 645 °C (1193 °F), and the diffusion of sulfur is much lower in cobalt than in nickel,[15] it is generally held that cobalt-base alloys offer better resistance to hot corrosion than nickel-base alloys. However, due to the complexity of the phenomenon and the importance of oxidation resistance, it is possible for nickel-base alloys to possess good hot corrosion resistance. This is illustrated by the data shown in Fig. 10.[16] Also evident from the figure is the superior performance of alloy 188 (39% Co) over that of alloy 25 (51% Co), which can be attributed to the superior oxidation resistance of alloy 188. In highly sulfidizing environments featuring low oxygen partial pressures, the effect of cobalt content is more clearly established, as shown in Fig. 11.[17] However, it is still possible for nickel-base alloys such as HR-160™ alloy to exhibit excellent sulfidation resistance due to alloying additions of chromium (28%) and silicon (2.75%) with reduced levels of cobalt.

5. Wear Properties

Wear is a very complex subject covering a broad variety of types and numerous variables that address both environmental
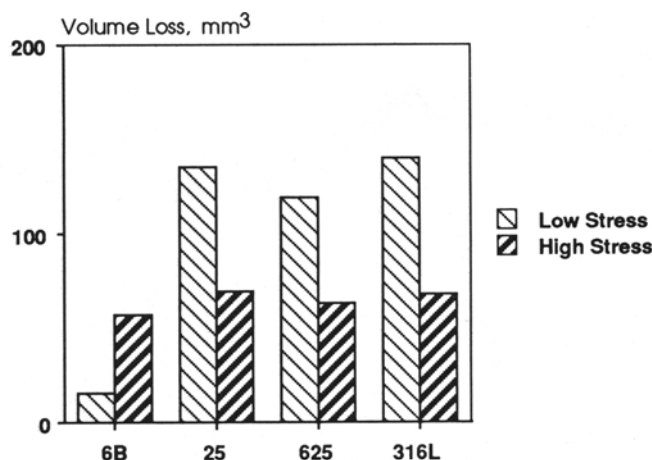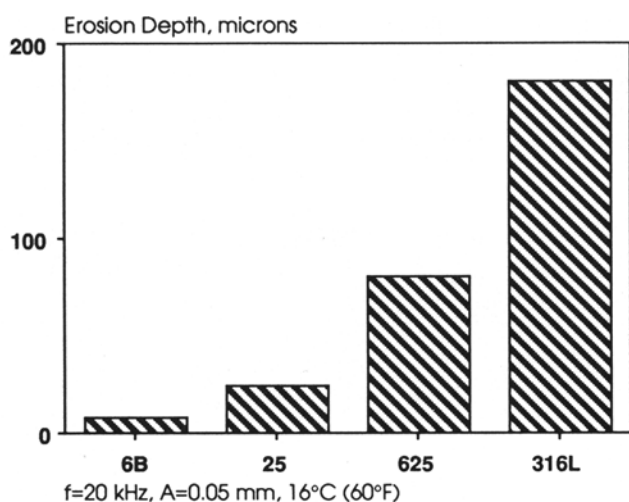
Fig. 12 Abrasion data for wrought alloys.

Fig. 14 Solid-particle impingement erosion data at room temperature.

Fig. 13 Cavitation erosion data for wrought alloys.

Table 6   Types of wear

Abrasive wear	Erosive wear
• High stress	• Solid particle
• Low stress	• Slurry
Sliding wear	• Liquid droplet
• Oxide control	• Cavitation
• Cold welding	
• Subsurface fatigue	
• Fretting	

and material characteristics. A simplified approach to the topic can be achieved by defining a set of types with subcategories as presented in Table 6.[18] Using this approach, the wear properties of cobalt-base alloys are briefly summarized in the following sections.

5.1 Abrasion

Low stress abrasion refers to a type of wear involving abrasive particles in which the particles remain intact. Earth moving would be one situation representing this type of wear. The presence of hard particles such as carbides appears to be quite beneficial in resisting this kind of wear,[19] so that an alloy like alloy 6B would be expected to perform well, as illustrated in Fig. 12. High stress abrasion refers to the wear situation in which the abrasive particles are crushed. In this case, the presence of carbides in the microstructure is not important, and as indicated in Fig. 12, cobalt-base alloys offer no advantage over nickel-base alloys or stainless steels.
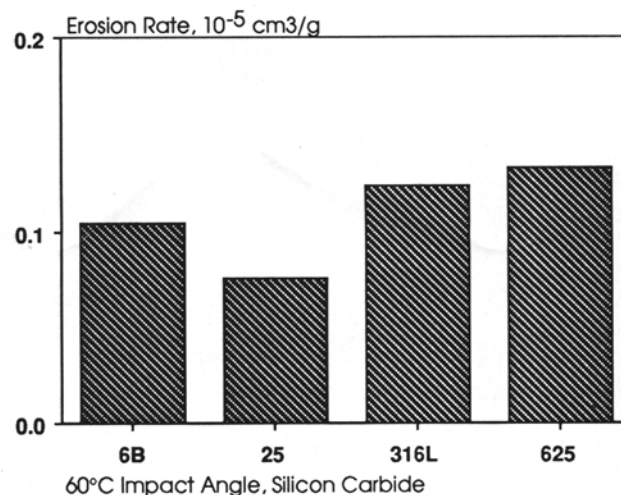
5.2 Erosion

Liquid drop impingement erosion and cavitation erosion are believed to involve the mechanism of fatigue on a microscopic scale.[20] Cobalt-base alloys with their low stacking fault energies, propensity toward deformation twinning, and stress-induced cph transformation appear to have an advantage in these situations. The cavitation erosion data presented in Fig. 13 confirm that this is indeed the case.

Solid-particle impingement erosion is quite complex and appears to depend greatly on system variables such as impingement angle, particle size and shape, particle hardness and velocity, and temperature. For ductile materials, impingement angles between 20 and 30° are most damaging, whereas normal impact (90°) is most damaging for brittle materials.[21] For metallic materials, it has been found that large precipitates in the microstructure tend to provide reduced resistance under conditions of solid particle impingement.[22] This behavior is illustrated by the data in Fig. 14, from which it can be seen that alloy 25 was more resistant than alloy 6B. It is also evident that differences between alloy bases are not very large. At elevated temperatures, the characteristics of the oxide films become important. As shown in Fig. 15, the best resistance was exhibited by a type 316L stainless steel, and cobalt-base alloys offered no advantage over nickel-base alloys.

It appears that slurry erosion has been studied on a very limited basis and is not well understood. Some parallels have been
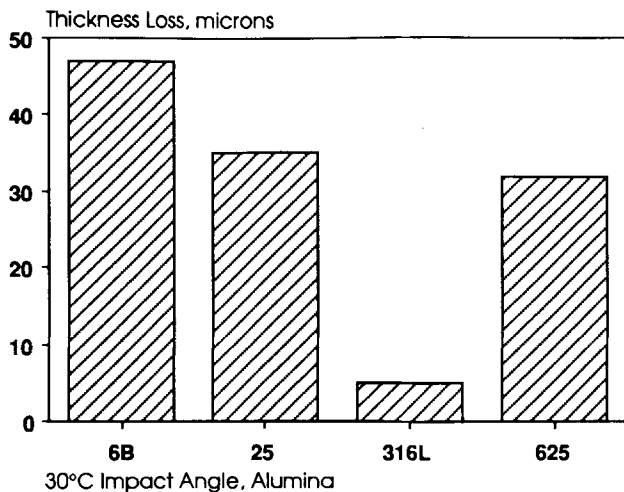
Thickness Loss, microns

30°C Impact Angle, Alumina

Fig. 15 Solid-particle impingement erosion data at 850 °C (1562 °F).

drawn between slurry erosion and low stress abrasion. However, slurry erosion appears to be quite different in that the liquid acts as a lubricant and a heat transfer agent.

5.3 Sliding Wear

Sliding wear in the absence of a lubricant is a complex phenomenon depending on variables such as loading, sliding velocity, and temperature. The extent of damage encountered can vary between seizure due to cold welding (galling) and minimal damage due to oxide control, in which case the oxides provide lubricant qualities. It appears that the damage often occurs as the result of microfatigue in the near-surface layers of the microstructure.[23] Again, the unique features of cobalt-base alloys offer an advantage in this type of wear. This is illustrated in Fig. 16 for the self-mated condition. The situation becomes more complicated when dissimilar materials are involved in the sliding couple, as shown for alloy C-276 in Fig. 16. The wear resistance of alloy 25 was substantially degraded, but some advantage is still observed for alloy 6B.

6. Concluding Remarks

Wrought cobalt-base alloys offer excellent high-temperature strength, resistance to sulfidizing environments, and resistance to many forms of wear. However, the development of new cobalt-base alloys has been severely hampered by economic and strategic vulnerability issues. The "cobalt crisis" that occurred in the late 1970s due to political unrest in the major African source caused a wave of substitution for cobalt-base alloys. In fact, the development of the nickel-base 230 alloy was one of the results. Despite the drive for substitution wherever possible, the fact remains that cobalt-base alloys offer unique combinations of properties not duplicated by other alloy systems. Therefore, the cobalt-base alloys will continue to be used for many years to come.
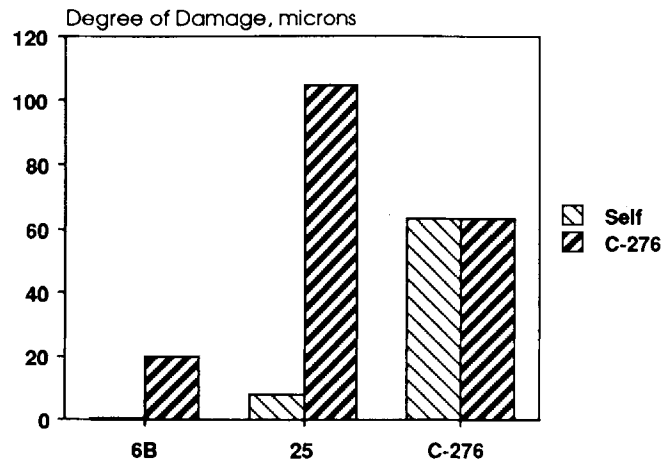
Degree of Damage, microns

Fig. 16 Galling data for wrought alloys.

References

1. C.P. Sullivan, M.J. Donachie, Jr., and F.R. Morral, *Cobalt-Base Superalloys—1979*, Cobalt Information Center, Brussels, Belgium, 1980
2. T.B. Massalski, H. Okamoto, P.R. Subramanian, and L. Kacprzak, Ed., *Binary Alloy Phase Diagrams*, Vol 2, 2nd ed., ASM International, 1990, p 1214-1215
3. C.T. Sims and W.C. Hagel, Ed., *The Superalloys*, John Wiley & Sons, 1972, p 145-174
4. H.M. Tawancy, V.R. Ishwar, and B.E. Lewis, On the fcc-hcp Transformation in a Cobalt-base Superalloy (HAYNES alloy No. 25), *J. Mater. Sci. Lett.*, Vol 5, 1986, p 336-341
5. A. Davin, V. LeRoy, D. Coutsouradis, and L. Harbaken, Comparison of Some Substitution Elements in Nickel and Cobalt, *Cobalt*, Vol 19, June 1963, p 51-56
6. F.C. Hagen et al., Mechanical Properties of a New Higher Temperature Multiphase® Superalloy, *Superalloys 1984*, Metallurgical Society of AIME, 1984, p 621-630
7. S. Takeda and N. Yukawa, *Nip. Kinz. Gakkai-ho*, Vol 6 (No. 11; 12), 1967, p 784-802; 850-855
8. D.I. Bardos, K.P. Gupta, and P.A. Beck, Ternary Laves Phases with Transition Elements and Silicon, *Trans. AIME*, Vol 221, Oct 1961, p 1087-1088
9. S.T. Wlodek, Embrittlement of a Co-Cr-W (L-605/Alloy, *Trans. ASM*, Vol 56, 1963, p 287-303
10. C.T. Sims, The Occurrence of Topologically Close-Packed Phases, in *The Superalloys*, John Wiley & Sons, 1972
11. R.B. Herchenroeder, S.J. Matthews, J.W. Tackett, and S.T. Wlodek, HAYNES alloy No. 188, *Cobalt*, Vol 54, Mar 1972, p 3-13
12. H.M. Tawancy, Long-Term Aging Characteristics of HASTELLOY alloy X, *J. Mater. Sci.*, Vol 18, 1983, p 2976-2986
13. H.M. Tawancy, D.L. Klarstrom, and M.F. Rothman, Development of a New Nickel-Base Superalloy, *JOM*, Vol 36 (No. 9), Sept 1984, p 58-62
14. C.T. Sims, A Contemporary View of Cobalt-Base Alloys, *JOM*, Vol 21, Dec 1969, p 27-42
15. C.T. Sims and W.C. Hagel, Ed., *The Superalloys*, John Wiley & Sons, 1972, p 317-339
16. G.Y. Lai, J.J. Barnes, and J.E. Barnes, "A Burner Rig Investigation of the Hot Corrosion Behavior of Several Wrought Superalloys and Intermetallics," ASME Paper 91-GT-21, June 1991
17. G.Y. Lai, A Sulfidation-Resistant Nickel-Base Alloy, *JOM*, Vol 41, July 1989, p 21-23

18. P. Crook and D.L. Klarstrom, "Advances in Alloy Design for Aggressive Wear Services," *ADVMAT/91, 1st Int. Symp. Environmental Effects on Advanced Materials*, NACE, June 1991

19. W.L. Silence, Effect of Structure On Wear Resistance of Co-, Fe-, and Ni-Base Alloys, *Wear of Materials*, ASME, 1977, p 77

20. D.A. Woodford, Cavitation-Erosion-Induced Phase Transformations in Alloys, *Metall. Trans.*, Vol 3, 1972, p 1137

21. C.J. Heathcock, B.E. Protheroe, and A. Ball, "The Influence of External Variables and Microstructure on Erosion by Solid and Liquid Impact," *ELSI 5 Proceedings*, Cambridge University Press, 1979, p 631

22. A. Ninham, The Effect of Mechanical Properties on Erosion, *Wear*, Vol 121, 1987, p 307

23. D.A. Rigney and W.A. Glaeser, *Wear of Materials*, ASME, 1977, p 41