ROLE OF REFRACTORY ELEMENTS IN COBALT-BASE ALLOYS

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ABSTRACT

Refractory metal elements play important roles
in the design and application of cobalt-base su-
peralloys. As in the case of nickel-base super-
alloys, alloying elements such as molybdenum and
tungsten are traditionally added to the cobalt
base for the purpose of providing solid solution
strengthening; however, the addition of various
refractory metals can profoundly influence the
basic physical metallurgy, mechanical behavior,
and environmental properties of cobalt-base ma-
terials. From this perspective, the major re-
search pertinent to a description of the effects
of refractory elements has been reviewed and sup-
plemented with limited results of recent previ-
ously unpublished work.

WHEN RECOUNTING THE HISTORY of the development
of modern-day cobalt-base "superalloys," most
authors are apt to begin with a reference to
the use of STELLITE® alloy No. 21 (or
"Vitallium") investment-cast turbosuperchar-
ger buckets in the early 1940s. However, the
origins of today's wrought and cast cobalt-base
high-temperature alloys can be traced back to
the work of Elwood Haynes in the early 1900s.
Haynes was the first to exploit the cobalt-
chromium-tungsten and cobalt-chromium-molybde-
num systems for their excellent hardness and
tool-material characteristics in the form of
the STELLITE alloy family, initially patented
in 1913.

The key aspect of this work was the addi-
tion of tungsten and/or molybdenum to the co-
balt-chromium alloys Haynes had patented ear-
lier in 1907. The true extent of the improve-
ment in elevated-temperature strength and wear-
resistance properties achieved with these re-
fractory metal additions was certainly not fully
appreciated until many years later. Yet, it is
clear that the roots of the present-day cobalt-
base superalloy family tree reach back to nearly
the turn of the century. The chemistries of
some important cobalt-base alloys are given in
Table 1.

The role of the refractory metal elements
molybdenum, tungsten, tantalum, columbium, and
vanadium in cobalt-base superalloys is at once
straightforward and complex. One hears the
alloys of this family commonly referred to as
"solid-solution-strengthened" materials, with
the primary role of refractory elements in the
alloys often described as being to provide such
strengthening. It is well known, however, that
these same refractory elements participate in
numerous phase reactions in cobalt-base alloys,
many of which can be used to provide various
forms of alloy property enhancement. Table 2
is a description after Sullivan, et. al.[2] of
the roles ascribed to those elements commonly
found in cobalt-base superalloys.

Among the effects associated with refrac-
tory metal elements in addition to solid-solu-
tion-strengthening are the strengthening effects
related to carbide precipitation and intermetal-
lic compound precipitation.

The purpose of this paper is to examine in
some detail the more complex roles played by re-
fractory metal elements in cobalt-base superal-
loys. This will be done from the viewpoint of
both the physical metallurgy of the materials
and their behavior in aggressive high-temperature
or wear environments. Among the many roles of
refractory elements in cobalt-base superalloys
which will be covered are: (1) Influence upon
the nature of carbides, (2) Stacking fault ener-
gy considerations, (3) Structure/mechanical pro-
perty effects, (4) Influence upon wear proper-
ties, and (5) Influence upon high-temperature
environmental properties.

PHYSICAL METALLURGY

A complete description of the physical me-
tallurgy of cobalt-base superalloys is beyond

TABLE 1

Composition of Cobalt-Base Superalloys

Tradename	Weight Percent											
	C	Cr	Ni	Mo	W	Cb	Ta	Ti	B	Zr	Fe	Others
STELLITE® alloy No. 31 (X-40)	0.50	25.5	10.5		7.5				0.01		2	
STELLITE alloy No. 21 ("Vitallium")	0.25	27	3	5							1	
WI52	0.45	21			11	2					2	
MAR-M® 302	0.85	21.5			10		9		0.005	0.2		
MAR-M 509	0.60	24	10		7		3.5	0.2		0.5		
FSX-414	0.35	29.5	10.5		7				0.01		2	
HAYNES® alloy No. 25 (L-605)	0.10	20	10		15							
HAYNES alloy No. 188	0.10	22	22		14							0.03 La
S816	0.38	20	20	4	4	4					4	
CM 7	0.10	20	05		15			1.3				0.5 Al
AIRESIST® 213	0.18	19			4.7		6.5			0.15		3.5 Al, 0.1 Y
UMCO-50 (HAYNES alloy No. 150)	0.10	28									21	
X-45	0.25	25.5	10.5		7				0.1		2	
J-1570	0.20	20	28		7			4			2	
J-1650	0.20	19	27		12	2		3.8	0.02			
STELLITE alloy No. 1	2.50	30			12							
STELLITE alloy No. 4	1.00	33			12							
STELLITE alloy No. 6	1.10	28			4							
STELLITE alloy No. 12	1.40	29			8							
STELLITE alloy F	1.70	25	22		12							
STELLITE alloy No. 694	0.85	28	5		19.5				0.04			1 V
STELLITE alloy No. 20	2.50	33			18							

the scope of this paper, and excellent comprehensive reviews of the subject are to be found in Wagner and Hall,[3] Moral, et al.,[4] Sims,[5] and Sullivan, et al.[2] Here we will present only a brief overview of the key consideration relevant to the physical metallurgy of the alloys, so as to better introduce the sections which follow.

Cobalt-base superalloys are normally characterized by a face-centered cubic (FCC) matrix containing second phases. Although the second phases are usually various different carbides, precipitation of other intermetallic compounds is also observed. An example of the profusion of phases sometimes encountered is given in Table 3 after the work of Takeda and Yukawa[6] on HAYNES alloy No. 25 (Alloy L-605).

TABLE 2

Effects of Several Elements in Cobalt-Base Superalloys[2]

Element	Effect
Chromium	Improves oxidation and hot-corrosion resistance; produces strengthening by formation of M_7C_3 and $M_{23}C_6$ carbides.
Molybdenum Tungsten	Solid-solution strengtheners; produce strengthening by formation of intermetallic compound Co_3M; formation of M_6C carbide.
Tantalum Columbium	Solid-solution strengtheners; produce strengthening by formation of intermetallic compound Co_3M and MC carbide; formation of M_6C carbide.
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.
Nickel	Stabilizes FCC form of matrix; produces strengthening by formation of intermetallic compound Ni_3Ti; improves forgeability.
Boron Zirconium	Produce strengthening by effect on grain boundaries and by precipitate formation; zirconium produces strengthening by formation of MC carbide.
Carbon	Produces strengthening by formation of carbides MC, M_7C_3, $M_{23}C_6$, and possibly M_6C.
Yttrium Lanthanum	Increase oxidation resistance.

TABLE 3

Phases Present in HAYNES alloy No. 25[6]

Phase	Crystal Structure	Lattice Parameters, Å
M_7C_3	Hexagonal (Trigonal)	a = 13.98 c = 4.53 c/a = 0.324
$M_{23}C_6$	Face-Centered Cubic	a = 10.55 ~ 10.68
M_6C	Face-Centered Cubic	a = 10.99 ~ 11.02
Co_2W	Hexagonal	a = 4.730 c = 7.700 c/a = 1.628
$\alpha-Co_3W$	Ordered Face-Centered Cubic	a = 3.569
$\beta-Co_3W$	Ordered Hexagonal	a = 5.569 c = 4.10 c/a = 0.802
Co_7W_6	Hexagonal (Rhombohedral)	a = 4.73 c = 25.5 c/a = 5.39
Matrix	Face-Centered Cubic	a = 3.569
Matrix	Hexagonal Close Packed	a = 2.524 c = 4.099 c/a = 1.624

No less than nine different phases were identified, including two matrix phases—one FCC and the other a close-packed hexagonal (HCP) phase.

Transformation of the FCC matrix to an HCP structure is known to occur in a number of cobalt-base superalloys. For example, the materials of the MULTIPHASE® alloy family derive their considerable strength in part from a strain-induced FCC to HCP transformation.[7-10] Substantial strengthening can be achieved when such

alloys are cold worked and aged, as illustrated by the data in Table 4 for HAYNES alloy No. 25 bar.[11]

TABLE 4

Tensile Properties for HAYNES alloy No. 25 Bar

Cold Worked 30 Percent and

Aged Six Hours at Various Temperatures

Aging Temperature (°F)	U.T.S. (ksi)	Y.S. (ksi)	Elongation (%)
As-Rolled	236	194	10
700	240	196	12
900	250	212	10
1125	251	242	9

Transformation of the FCC matrix to an HCP structure is closely related to the common occurrence of stacking faults in many cobalt-base superalloys. Stacking faults and stacking fault energy considerations are dealt with later in this paper.

The majority of commercial cobalt-base alloys derive their strength at high temperatures from a combination of solid solution strengthening, from precipitation of carbides, and, to a lesser extent, from precipitation of intermetallic compounds. The solution strengthening of cobalt-chromium alloys through ternary additions of molybdenum, tungsten, columbium, and tantalum has been studied by Rausch, et. al.[12] and Drapier, et al.[13] Rausch established that all of these elements provide substantial increases in 925°C (1700°F) yield strength when added to cobalt-base alloys containing 15% to 25% chromium. This is shown clearly in Figure 1. Solubility limits at 1200°C (2190°F) for these same elements in the cobalt-chromium system were determined by Drapier, et al. The cobalt-rich corner of a superimposition of the 1200°C ternary isothermal sections is shown in Figure 2.

Various different carbides have been identified in current commercial cobalt-base alloys. A summary of the various types observed for representative alloys has been derived from a variety of sources and is presented in Table 5. In discussing the role of carbides in cobalt-base superalloys, it is necessary to draw the distinction between primary carbides present in the cast or wrought materials in the as-annealed or as-produced condition and those carbides which precipitate upon subsequent purposeful heat treatment, cooling from the heat treatment, or service thermal exposure. From the work of
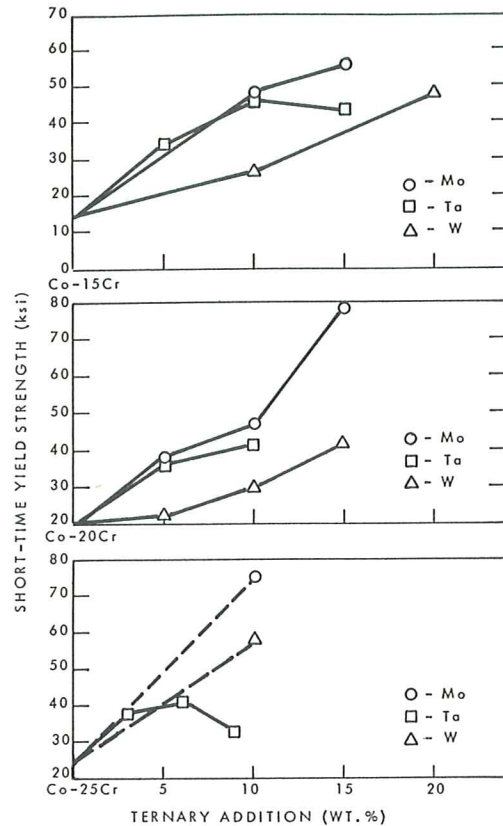

Fig. 1: The effect of molybdenum, tantalum, and tungsten additions on the 925°C (1700°F) short-time yield strength of Co-Cr base alloys. After Rausch, et al.[12]
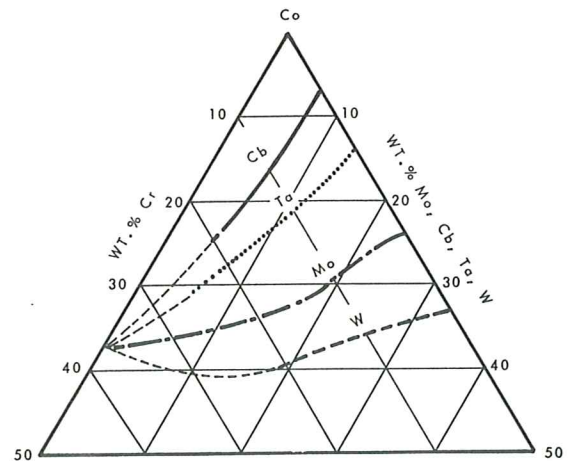

Fig. 2: 1200°C (2190°F) isothermal sections of the Co-Cr-X systems (X = Mo, W, Cb, Ta) showing cobalt-base solid-solution field boundaries. After Morral, et al.[4]

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TABLE 5

Carbide Phases Reportedly Present in Various Cobalt-Base Superalloys

Tradename	
S 816	MC, $M_{23}C_6$, M_6C
HAYNES alloy No. 25	M_6C, $M_{23}C_6$
STELLITE alloy No. 31 (X-40)	M_7C_3, M_6C, $M_{23}C_6$
X-45	$M_{23}C_6$
STELLITE alloy No. 21 ("Vitallium")	M_7C_3, $M_{23}C_6$, M_6C, Cr_3C_2
J-1650	M_6C, $M_{23}C_6$, Cr_3C_2
J-1570	M_6C
AIRESIST 213	MC
MAR-M 302	MC, M_6C, $M_{23}C_6$
MAR-M 509	MC, $M_{23}C_6$
STELLITE alloy No. 6	$M_{23}C_6$, Cr_7C_3, M_6C
HAYNES alloy No. 188	M_6C, $M_{12}C$, $M_{23}C_6$
STELLITE alloy F	M_7C_3, M_6C, $M_{12}C$, $M_{23}C_6$

Clauss and Weeton,[14] Morrow, et al.,[15] Löbl,[16] and Zordan,[17] it is apparent that the type and morphology of primary carbides can substantially influence the elevated temperature properties and wear resistance of cobalt-base superalloys.

Many investigators have also examined the effects of secondary carbide precipitation upon cobalt alloy properties. The association of strengthening of MAR-M 509 with precipitation of $M_{23}C_6$ carbides during aging has been well documented.[18-20] Work on less complex cobalt-base systems has also been extensive, clearly establishing a strong relationship between secondary carbide precipitation and property changes.[21-25] Figure 3 illustrates the hardening response associated with $M_{23}C_6$ carbide precipitation during aging of Co-25Cr-0.26C and Co-10Ni-25Cr-0.25C alloys.[23]
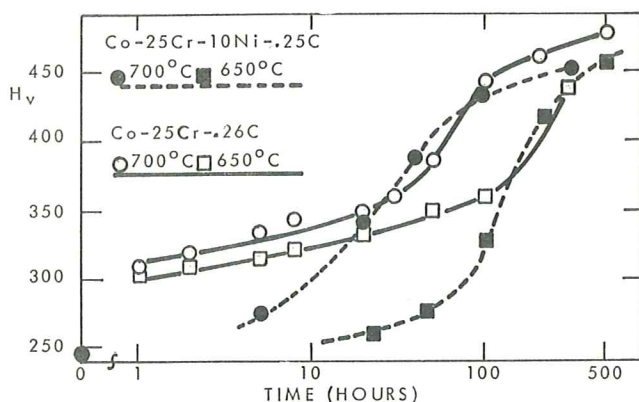
Intermetallic compound precipitation in cobalt-base superalloys is a subject which has been as well investigated as carbide reactions, though perhaps less productively in terms of commercial exploitation. The wealth of possible intermetallic compounds available for potential use in strengthening cobalt-base superalloys is evident from an examination of Table 6, adapted from Drapier, et al.[13] and others.

TABLE 6

Intermetallic Compound Types
in Cobalt-Base Superalloys

Compound	Structure
$Co_3(Mo, W, Ta, Cb)$	HCP, Ordered
Co_3Ti, β Co_3Ta	FCC, Ordered
$Co_2(Mo, W, Ta, Cb)$	Hexagonal, Laves Phase
$Co_7(Mo, W)_6$	Rhombohedral-Hexagonal, Mu Phase
$Co_2(Ta, Cb, Ti)$	Cubic, Laves Phase
$Co_2(Mo, W)_3$	Sigma Phase
$CoAl$	Cubic, Ordered
$(Co, Ni)_3(Al, Ti)$	FCC, Ordered
Co_3Ti	HCP

Despite this, generation of an intermetallic precipitate combining the high-temperature stability and versatility of the analogous $Ni_3(Al,Ti)$ γ' phase in nickel-base alloys has proven to be a largely elusive goal. Alloys employing such phase precipitation as the principal mode of high-temperature strengthening have yet to gain much commercial acceptance, though substantial research has been performed in this area.[26-32]

CARBIDES

The type and morphology of primary carbides can substantially affect the properties of cobalt-base superalloys. The influence of refractory metal additions to cast cobalt-base alloys upon carbide morphology and alloy properties has been thoroughly explored.[14-17, 33-39] Morrow, et al.[15] evaluated the effects of substituting molybdenum for tungsten in cast alloys FSX-414 and MAR-M 509. They found that, for MAR-M 509, substitution on an equivalent atomic percent basis produced more rounded, discrete, and less continuous MC script carbide structure. This was accompanied by a slight increase in both tensile and stress rupture ductility, which was also observed for the molybdenum-substituted FSX 414 despite no apparent refinement of the primary carbide structure. These results are in basic agreement with the earlier work of Griffiths and Phelps[33] on substitution of molybdenum for tungsen in

Fig. 3: Hardness versus aging time data for Co-25Cr-0.26C and Co-25Cr-0.25C alloys. After Beaven, et al.[23]

STELLITE alloys No. 4 and No. 7, yielding
STELLITE alloys No. 5 and No. 8, respectively.
Taken together, the studies indicate that, on
an atomic-percent basis, molybdenum and tung-
sten are similar in their effect upon carbide
structure.

The influence of tungsten on the micro-
structure and wear properties of alloys in the
STELLITE alloy No. 12 family (31.5%Cr-1.5%C-
0.5%Mn-0.8%Si-2%Fe-0% to 16% W-Balance Co) was
examined by de Brouwer, et al.[34] Although the
effect of increasing tungsten levels upon car-
bide morphology was not reported, x-ray dif-
fraction analysis of extracted residues was
performed. The results, which are given in
Table 7, show that M_7C_3 is the only carbide
formed upon solidification of the alloys con-
taining up to 8% tungsten.

TABLE 7

Carbides Identified by X-Ray Analysis of

STELLITE alloy No. 21-Type Materials[34]

| Alloy, weight percent | | | | Carbides Detected |
Cr	C	W	Co	
31.5	1.5	-	66.7	M_7C_3
31.5	1.5	4	62.7	M_7C_3
31.5	1.5	8	58.7	M_7C_3
31.5	1.5	12	54.7	$M_7C_3 + M_6C$
31.5	1.5	16	50.7	M_6C

At the 12% tungsten level a mixture of M_7C_3 and
M_6C carbides is observed. When the tungsten
level is raised to 16 percent, only M_6C-type
carbides are found in the as-cast material.

This change in the carbide type with in-
creasing tungsten found by de Brouwer, et al.
was reportedly accompanied by an appreciable
lowering in the alloy liquidus temperature with
little change in the solidus. This is shown in
Figure 4, and it implies a finer dendrite
structure for the high-tungsten compositions.
More recent work by Durand-Charre,[35] however,
reports little change in the liquidus tempera-
ture for tungsten variations bwtween 8.4 and
14.9 percent in STELLITE alloy F-type materials
(1Si-25Cr-22Ni-1.5C-W-Co Balance).

Hot hardness was also evaluated by de
Brouwer, et al. for the 0% to 16% tungsten
variations on STELLITE alloy No. 12 and the
results related to performance in a 600°C
(1110°F) metal-to-metal wear test. Hardness
at 600°C (1110°F) as a fraction of room tempera-
ture hardness is plotted versus tungsten content
in Figure 5b, and weight loss in the wear test
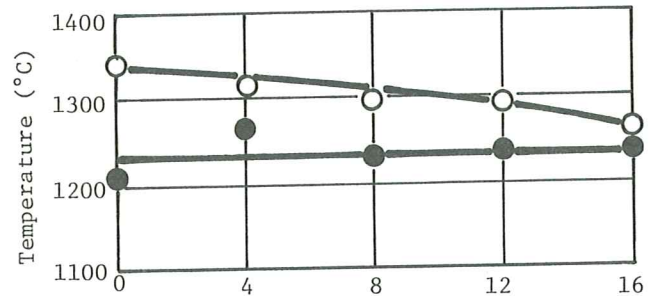is plotted versus tungsten content in Figure 5a.

Fig. 4: Effect of tungsten content on the
solidification temperatures of STELLITE 12-type
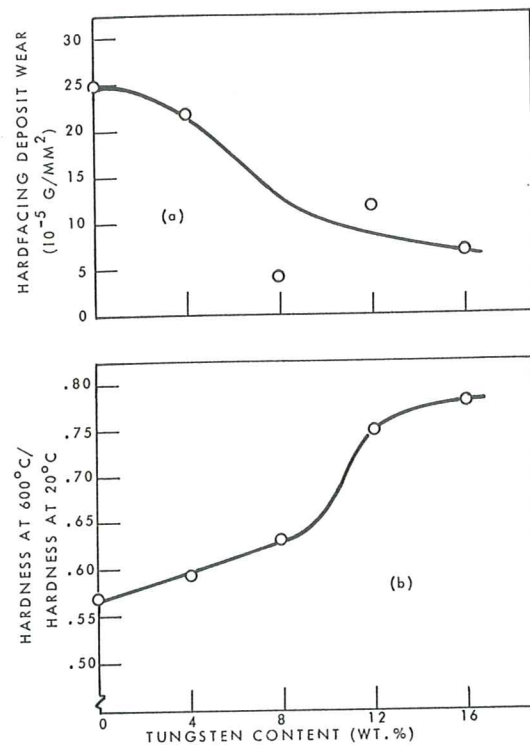alloys (1.5% C). After de Brouwer and
Coutsouradis.[34]

Fig. 5: (a) 600°C metal-to-metal wear behavior
of alloys as a function of tungsten content.
Data taken from de Brouwer and Coutsouradis.[39]
(b) Fraction of room temperture hardness retained
at 600°C as a function of tungsten content in
STELLITE alloy No. 12 materials.

A combined plot of wear weight loss versus
hardness at 600°C (1110°F), including addi-
tional data reported by de Brouwer, is shown
in Figure 6. The authors note that tungsten is
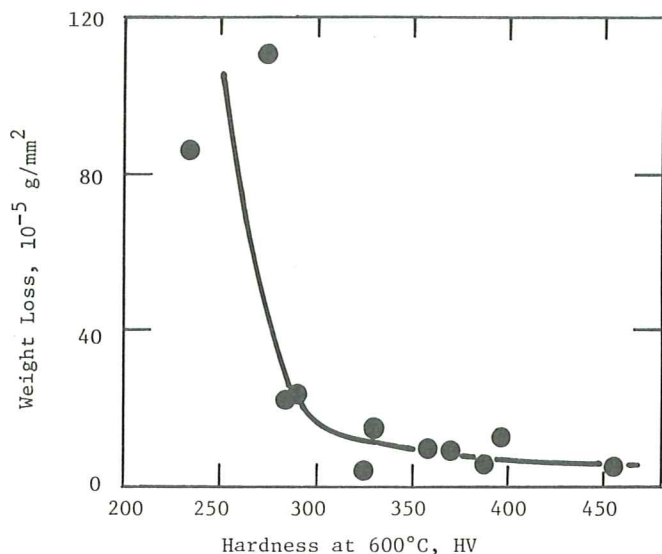indispensible to ensure that the alloys retain

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Fig. 6: Wear of STELLITE 12-type alloy deposits as a function of their hardness at 600°C. After de Brouwer and Coutsouradis.[24]

Alloy	Volume Loss (mm^3)	Hardness (Rockwell C)
STELLITE alloy No. 20	23.3	53
STELLITE alloy No. 1	51.7	54
STELLITE alloy No. 694	68.2	50
STELLITE alloy No. 6	63.8	40

a high hardness at elevated temperatures. The relationship of wear resistance to hardness, though not absolute, also indicates the need for high tungsten levels.

That the hardness is not an absolute guide to the wear resistance of cobalt-base super-alloys is illustrated by the recent work of Zordan.[17] Figure 7 contains photomicrographs which depict the as-cast microstructures of four different cobalt-base alloys with different carbon and tungsten contents. Data relating the hardness and abrasive wear resistance of these same four alloys is presented in Table 8. Clearly, hardness is no guide to either expected wear performance or microstructural condition in this case. The finer particle size and interparticle spacing combined with the increased amount of M_7C_3 and M_6C carbides

in STELLITE alloy No. 20 probably contribute to its superior wear performance.

The influence of the addition of elements such as columbium, tantalum, zirconium, and titanium upon the primary carbide structure of cobalt-base alloys has also been thoroughly explored.[36-39] Youdelis and Kwon[36] found that additions of up to 2.3% columbium or 3.25% tantalum dramatically refine the primary carbide size in cast STELLITE alloy No. 21 by promoting the formation of fine MC carbides in place of coarser $M_{23}C_6$ carbides. Drapier, et al.[39] observed similar behavior for 1.5% columbium additions to iron-base alloys containing 25% chromium, 52% cobalt/5% nickel, 42% cobalt/9% nickel, 32% cobalt/12% nickel, all with 0.25% carbon. The carbide refinement was accompanied by a substantial increase in stress/rupture strength, as shown in the Larson-Miller plot in Figure 8.

Fig. 7: Comparison of the microstructures of four alloys with varying tungsten and carbon content; STELLITE alloys No. 20 (a), No. 1 (b), No. 694 (c), and No. 6 (d). Light etching particles are M_7C_3. Dark etching particles are M_6C. After Zordan.[17]
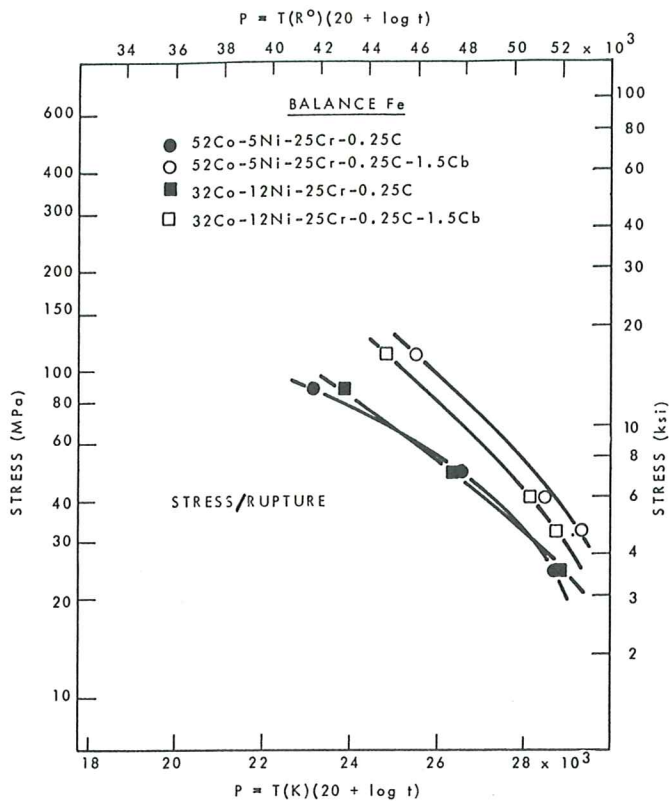
Fig. 8: Stress rupture properties of Fe-Co-Ni-Cr-C alloys with added columbium. Data from Drapier, et al.[39]

Fig. 9: Effect of 0.4% Cb and 0.83% Ta additions upon the stress/rupture properties of Alloy X-40. Adapted from Davin, et al.[38]

Earlier work by the same authors[38] for 0.83% tantalum and 0.4% columbium additions to Alloy X-40 with 0.5% carbon had yielded comparable improvements in rupture properties, as shown in Figure 9.

Fukui, et al.[37] performed the same type of studies involving small titanium, columbium, and zirconium additions to Cast FSX-414 alloy. They found that much smaller eutectic carbides were formed when, for example, 0.15% titanium, 0.19% zirconium, and 0.24% columbium were added to the base alloy. Optimization of 980°C (1800°F) rupture strength, however, was found to be possible only by controlling the ratio of carbon content to the amount of MC carbide stabilizers added. This is illustrated by the plot in Figure 10 of 1000-hour rupture strength at 980°C (1800°F) versus the atomic weight ratio of (Ti + Cb + Zr)/C. This shows that optimum rupture life is obtained at an atomic weight ratio of MC stabilizer element to carbon contained of about 0.3. Fukui concludes that the decrease in rupture strength at higher ratios is due to excessive primary MC stabilization, depletion of matrix carbon content, and reduction of in-service strengthening by $M_{23}C_6$ carbide precipitation.

Contrary results were reported by Davidson,[24] who examined the aging characteristics of HAYNES alloy No. 25 and molybdenum-substituted alloys of the same family
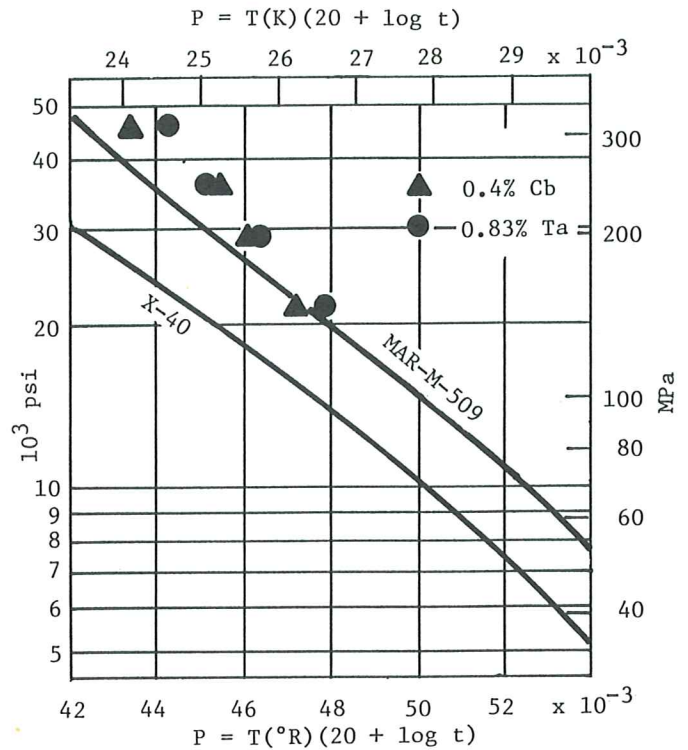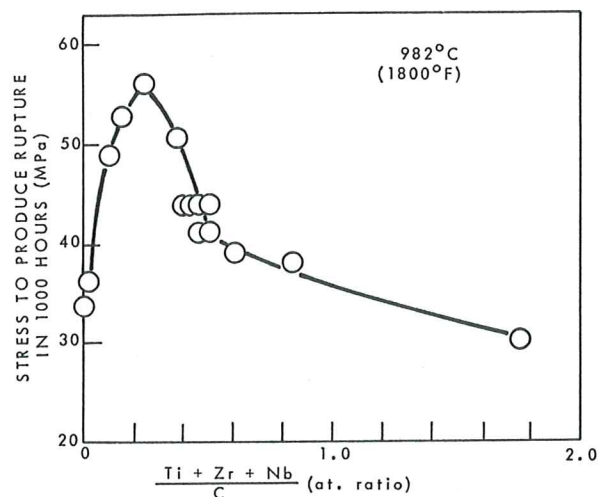

Fig. 10: Relationship between 982°C (1800°F) stress rupture strength of FSX-414 alloys modified with various MC formers and the ratio of such elements to the carbon content (atomic percent basis). After Fukui, et al.[37]

with additions of titanium and columbium. In his studies involving 16-hour exposures at temperatures between 650°C (1200°F) and 1100°C (2015°F) Davidson observed that 1-percent additions of columbium or titanium to the molybdenum-substituted heats shifted the peak in the

hardening response upward from 700°C (1290°F) to 800°C (1470°F). He related this shift to the observed precipitation of secondary columbium-rich, MC carbides, which appeared in a 200Å thick platelet morphology accompanying the more profuse globular $M_{23}C_6$ precipitation. The CbC platelets apparently precipitated preferentially upon dislocations, and being finer in size and more thermally stable, could logically be expected to improve the strength of the material more efficiently than the larger $M_{23}C_6$ precipitates.

This secondary precipitation of MC carbides and associated strengthening was also observed by Ramaswamy, et al.[21] for Co-20Cr-10Ni-5Ta alloys with from 0.13% to 0.29% carbon. They report that TaC precipitation occurs upon aging in the range from 650°C to 850°C (1200°-1560°F), wih repeated precipitation upon dislocations giving rise to the formation of HCP stacking faults in the FCC matrix. TaC precipitates also form preferentially upon stacking faults induced by prior cold work, with the aged hardness increasing appreciably as a result, much as in the case of cold-worked and aged HAYNES alloy No. 25.

STACKING FAULTS

The role of stacking fault energy in nickel-base superalloys is perceived to be straightforward, with the addition of those elements which promote lower fault energy leading to high strength. In cobalt-base alloys the situation is complicated in that low fault energy can also lead to the FCC→HCP allotropic transformation which weakens cobalt-base alloys. As will be discussed, a balance is required.

The occurrence of HCP stacking faults in otherwise FCC matrix cobalt-base supperalloys is widely known, and the relevance of stacking fault energy considerations to the occurrence of the FCC → HCP allotropic transformation has been discussed by several authors.[2,4,5,41] The role of various elements in the occurrence of the allotropic transformation has been reviewed by Sims[5] and in detail by Giamei, et al.[41] In general, it is proposed that refractory metals such as molybdenum and tungsten tend to stabilize the HCP structure while others such as tantalum and columbium appear to be FCC stabilizers. This is illustrated by the diagram presented in Figure 11, after Sims.[5]

The relationship between stacking fault energy and the allotropic transformation is that the fault energy approaches zero when the FCC matrix transforms allotropically to HCP. Sullivan, et al.[2] point out an important consideration in the fact that, even in the supposedly stable FCC temperature regime, the stacking fault energy is sufficiently small to allow for stacking fault formation to appreciably influence creep properties. Sims proposes that the diagram shown in Figure 11 relating the influence of various elements upon the allotropic transformation can also be used as at least a general qualitative guide to the effects of
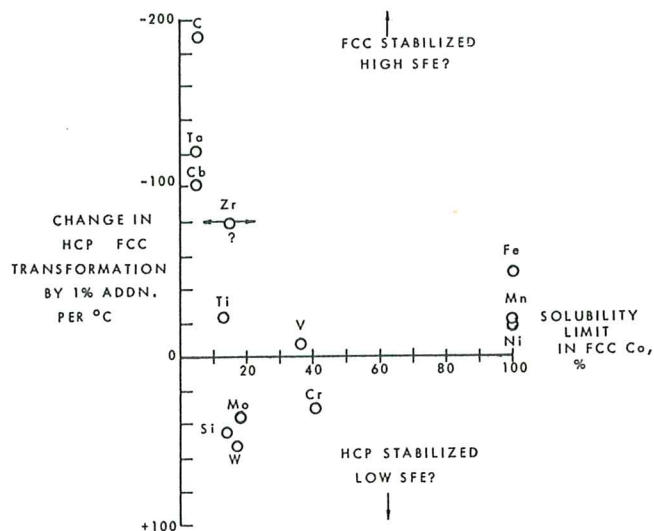

Fig. 11: Effect of alloying additions (in atomic percent) on the HCP→ FCC transformation in cobalt as a function of solubility in FCC cobalt. After Sims.[5]

alloying additions on stacking fault energy. He further cautions that, for cobalt-base alloys, stacking faults warn of proximity to the HCP structure, and can be regarded as a precursor to more massive HCP formation.

The relationship between the chemistry of cobalt-base alloys and stacking fault formation is still a relatively complex issue, however. For example, Drapier and Coutsouradis[42] examined Co-Cr-Ta alloys aged at 700°C (1290°F). As mentioned previously, tantalum might be expected to raise the stacking fault energy of Co-Cr alloys; however, in this case, precipitation of Co_3Ta was observed, and as a consequence, the density of stacking faults in the tantalum-depleted matrix increased substantially during aging. A similar phenomenon was noted by Ramaswamy, et al.[21] for the Co-20Cr-10Ni-5Ta-0.13 to 0.29C alloys they studied, although in this case TaC precipitation on dislocations led to the fault formation.

Such precipitation-induced fault formation in cobalt-base alloys is well documented in the literature.[21-25,42,43] Beaven, et al.[23] describe an interesting case for a Co-25%Cr-0.26%C alloy. Material predeformed 10 percent displayed some initial transformation to the HCP phase. Aging was performed at 650°C (1200°F) for up to 500 hours, and, in the early stages of aging, $M_{23}C_6$ precipitation was observed to occur upon the Frank partial dislocations bounding the individual stacking faults. With longer times, recrystallization and carbide coarsening were observed to occur simultaneously, eventually resulting in the complete transformation of the matrix to a fault-free HCP structure after 500 hours.

The importance of stacking fault energy considerations in the wear properties of cobalt-base alloys has also been recognized.[44] Low stacking fault energy appears closely related

to superior galling performance. Dennis and Still[45] evaluated the wear resistance of pure Co-Mo and Co-W electrodeposited coatings on forging dies, and they found a clear relationship between the wear volume measured on the forging dies and the percent of tungsten or molybdenum in the cobalt alloy coating. This is shown in Figure 12.
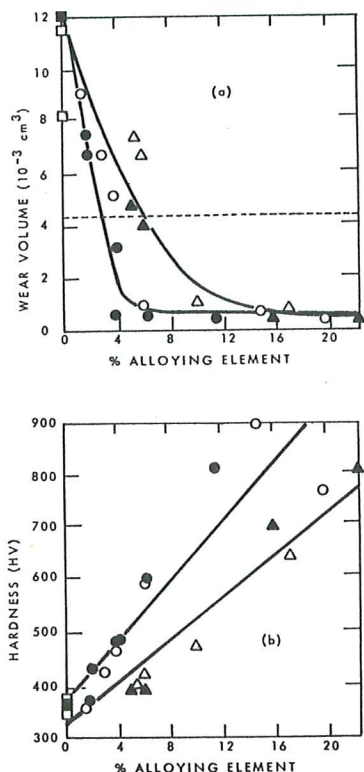

Fig. 12: Relationship between the alloying element content of Co-Mo and Co-W die coatings and their degree of wear and hardness after forging 1000 billets. After Dennis and Still.[45]

Surprisingly, while hardness increased continually with increasing tungsten or molybdenum content to very high levels, wear resistance appeared to stabilize at an optimum low level after a content of about 4%-6% molybdenum or 10%-15% tungsten was reached. Since both of these alloys were pure binary, single-phase materials, it might be suggested that the existence of an optimum level of molybdenum or tungsten addition for achieving improved wear resistance could be related to a critical low level of stacking fault energy.

INTERMETALLIC COMPOUNDS

The strengthening of cobalt-base superalloys by precipitation of intermetallic compounds has remained very much secondary in importance compared to carbide strengthening. Nevertheless many intermetallic compounds have been identified in cobalt-base alloys, and several investigations have been undertaken in the past to establish which of these phases

hold the most promise for commercial exploitation. Some of the intermetallic compounds which show some value in this respect are Co_3W and Co_3Mo (both ordered hexagonal), Co_3Ta (either metastable ordered cubic or rhombohedral forms), Co_3Ti (ordered cubic), and Co_2Cb (Laves hexagonal).

An excellent summary of the precipitation hardening characteristics of intermetallic compounds in Co-Cr-W, Co-Cr-Mo, Co-Cr-Ta, and Co-Cr-Cb alloys has been presented by Drapier, et al.[13] The 100-hour aging response of selected alloys at various temperatures is shown in Figure 13.
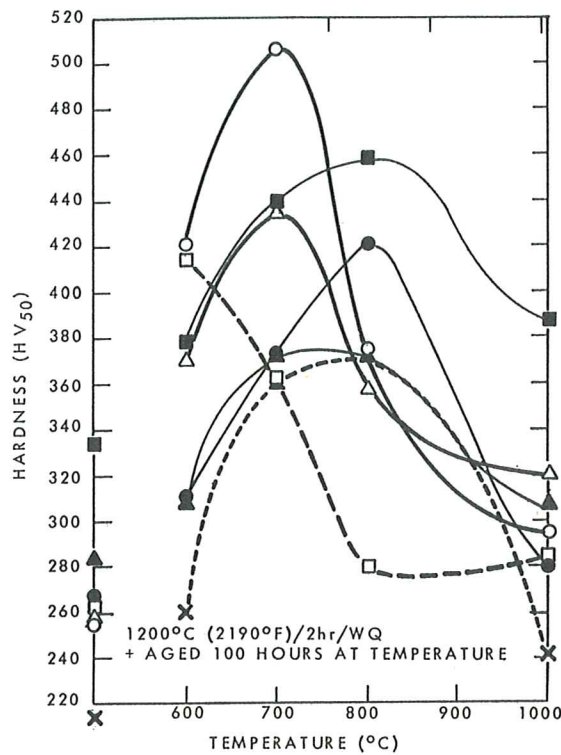
WEIGHT PERCENT		
Co	Cr	X
70	15	15 W
75	11	14 Mo
70	17	13 Mo
67	18	15 Mo
82	8	10 Ta
77	15	8 Ta
90	5	5 Cb

Fig. 13: Hardness response for 100-hour aging of ternary Co-Cr alloys. After Drapier, et al.[13]

Substantial strengthening is evidenced in all of these systems, yet the strength is readily lost at temperatures above the range from 750° to 850°C (1380° to 1560°F) as a result of overaging.

A great deal of the effort expended in the search for a stable, high-temperature strengthening precipitate in cobalt-base alloys has been

directed at the Co_3Ti analog of the γ' precipitate in nickel-base superalloys.[26-32] The main problem is the long-term stability of this initially coherent, ordered FCC precipitate at temperatures above 750°C (1380°F). A number of investigators have examined the influence of refractory metal additions to Co-Cr-Ti or Co-Ni-Cr-Ti alloys, with mixed results. Drapier, et al.[30] reported that transformation of the ordered FCC Co_3Ti γ' precipitate in Co-Cr-Ti alloys to an HCP structure is promoted by the addition of molybdenum in excess of 3% to 5%, with the same effects expected for the other refractory elements. Similar results are reported by Viatour, et al.[29] who observed discontinuous, lamellar HCP phase precipitation in Co-Ti-Mo and Co-Ti-W alloys aged at 700°C (1290°F). Kinetics of the precipitation were observed to increase with increasing tungsten content in those alloys.

A different behavior was noted by Viatour, et al. for ternary additions of tantalum to Co-Ti alloys. Here discontinuous lamellar precipitation was not observed at 700°C (1290°F), but only at 800° and 900°C (1470° and 1650°F). At 1000°C (1830°F) platelets of an intermetallic HCP precipitate were found, likely a version of the β Co_3Ta-type structure. This difference for tantalum was not found to carry over to Co-Cr-Ti-X alloys investigated, however, where additions of over 1 atomic percent of molybdenum, tungsten, or tantalum were all found to promote formation of the lamellar phase upon aging at 700°C (1290°F). Walder and Marty[31] investigated the effects of minor columbium additions to a Co-16%Cr-4%Ti-3%Mo alloy, and although no microstructural results were reported, it is clear from the hardness data that columbium does not increase the precipitate stability temperature range beyond the 750°C (1390°F) of the base alloy.

Results obtained relative to more complex systems have been fewer and perhaps less illuminating as far as understanding structure/composition/property relationships in these alloys. Further investigation by Drapier and Coutsouradis[42] into the Co-Cr-Ta systems modified with nickel, vanadium, aluminum, and titanium demonstrated that an effective strengthening ordered FCC Co_3Ta-type precipitate could be obtained with aging at least up to 800°C (1470°F). At aging temperatures approaching 900°C (1650°F), however, the rhombohedral Co_3Ta was always observed.

Perhaps the most systematic studies performed upon complex systems were done by Acuncius.[28] Taking the approach that analagous nickel-base superalloys make simultaneous use of γ'-forming elements, solid solution strengtheners, and carbide formers, Acuncius evaluated complex multicomponent cobalt-base alloys containing as many as 11 elements. The main thrust of this work was still directed at increasing the stability of the γ'-type precipitate. In this respect he concludes that the greatest improvement in the stability of the γ' phase (in a base alloy containing nominally 20%Cr-15%Ni-3%Ti-3%Al-Balance Co) is achieved through the addition of columbium and/or tantalum. This is readily apparent from an examination of Figure 14, which depicts the stress rupture properties of alloys containing various refractory metal combinations.
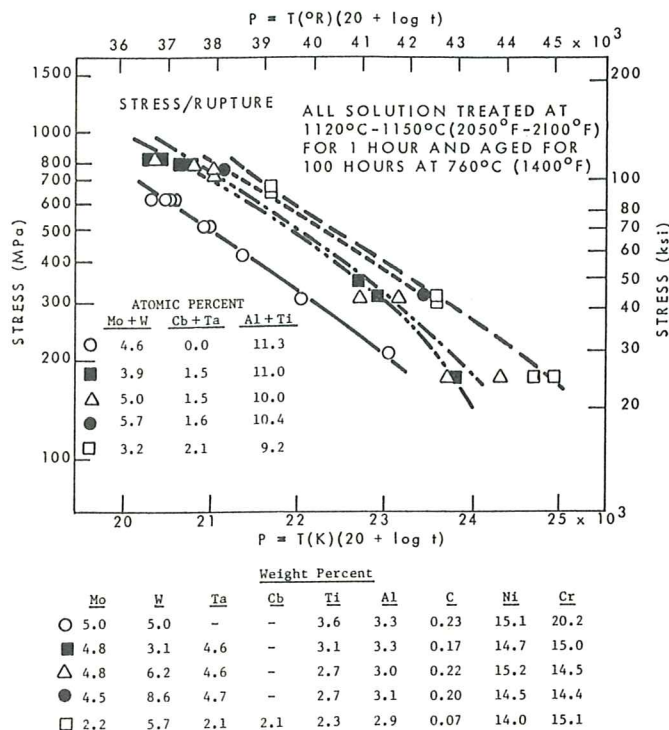

Fig. 14: Effect of various refractory metal element combinations upon the stress rupture properties of a cobalt-base alloy. Data from Acuncius.[28]

Herchenroder[46] observed a basically similar trend in alloys containing 21%Cr-24%Ni and varying amounts of molybdenum, tungsten, and tantalum, but allowed to age harden during testing (test performed upon as-solution-treated material). He noted a synergism between the tungsten and tantalum content, claiming a ratio of tantalum to tungsten between 1.5 and 2.5 as being optimum. This is illustrated by the data in Figure 15. The disadvantageous effect of molybdenum addition was also noted.

One novel use for intermetallic compound precipitation in cobalt-base alloys has been the development of the TRIBALOY® series of commercial wear-resistant materials. These alloys, such as TRIBALOY alloy No. T-800 (28%Mo-17%Cr-3%Si-Balance Co), develop massive Laves phase in an HCP matrix. The hardness of the Laves phase is about 1100 on the Vickers scale, which compares quite favorably with that of typical tool steels (950 Vickers). Such alloys are ideal
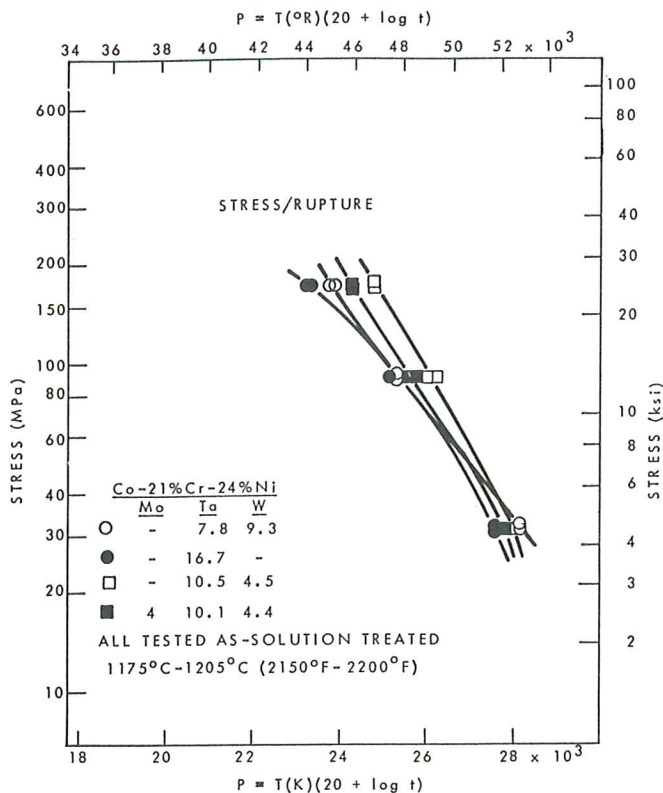
Fig. 15: Stress-rupture properties of Co-Cr-Ni alloy containing various refractory metal additions. Data taken from Herchenroeder.[46]

TABLE 9

Role of Alloying Additions to

Cobalt-Base Materials in Oxidation[5]

Alloying Element	Probable Effect of Addition on the Oxidation Behavior of a Co(20–30)Cr Base
Titanium	Innocuous at Low Levels
Zirconium	Innocuous at Low Levels
Carbon	Slightly Deleterious; Ties Up Chromium
Vanadium	Harmful, Even at 0.5%
Columbium	Harmful, Even at 0.5%
Tantalum	Beneficial to Moderate (< 5%) Levels
Molybdenum	Harmful; Forms Volatile Oxides
Tungsten	Innocuous below ~ 1800°F (1000°C), Harmful > 1800°F (1000°C); Forms Volatile Oxides
Yttrium	Beneficial; Improves Scale Adherence
Nickel	May Be Slightly Deleterious
Manganese	Beneficial; Induces the Formation of Spinels
Iron	Tends To Induce Spinel Formation

choices for wear applications in poorly or non-lubricated, high-temperature environments.[47] Currently, such materials are being considered for cylinder sleeve materials in advanced diesel engines.

ENVIRONMENTAL RESISTANCE

The role of various elements in the processes of oxidation and hot corrosion of cobalt-base superalloys has been generally summarized by Sims,[5] and more specifically addressed by Beltran.[48] Table 9 is a summary of Sims's catagorization of elemental effects in oxidation. It is evident from this summary that he considers all refractory elements harmful to some degree, with the exception of tantalum. This is in basic agreement with the data of Davin, et al.,[49] who found molybdenum and columbium to be particularly deleterious in Co-30%Cr-X alloys tested in still air for five hours at various temperatures. Beltran[48] ascribes the inferiority in oxidation behavior of Alloy WI-52 compared to Alloy MAR-M 509 to the columbium content of the former versus the tantalum content of the latter. He also points to the 9% tantalum in MAR-M 302 as the probable reason for that alloy's excellent relative resistance to oxidation, citing a comparison of all of these alloys made by Wheaton in earlier work.[50] This comparison is presented in Figure 16. Interestingly enough, Boone and

Sullivan[52] equate the inferiority in thermal fatigue resistance of cast Alloy WI-52 in comparison to MAR-M 302 to the poorer oxidation resistance of the columbium-bearing WI-52, though differences in carbide morphology were also cited as being related to the degree of oxidation penetration.

The beneficial effects of tantalum as opposed to columbium are also demonstrated in the work of Irving, et al.[51] for Co-20%Cr-X alloys containing nominally 4%, 7% and 10% columbium or tantalum. Tests were performed in oxygen and air at temperatures between 900° and 1100°C (1650° and 2010°F) for up to 350 hours. The results illustrate that columbium accelerated the oxidation rate while tantalum proved beneficial at all temperatures. This is shown by the curves in Figure 17 for oxidation studies conducted at 1000°C (1830°F). The authors relate the ability of the tantalum-containing alloys to form a complex oxide, $CrTaO_4$, to the observed better oxidation resistance. An analogous columbium-bearing oxide was not observed. Beltran[48] similarly warns against large additions of vanadium.
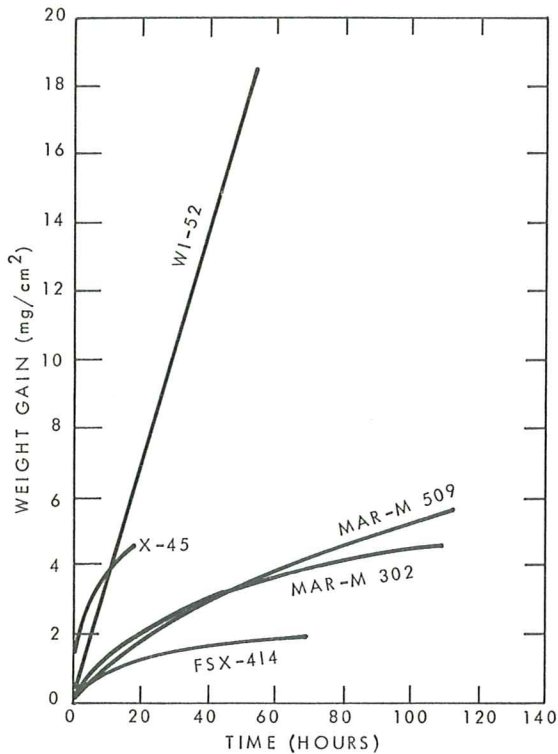
111

Fig. 16: Static oxidation of selected cobalt-base superalloys at 1095°C (2000°F). After Beltran.[48]
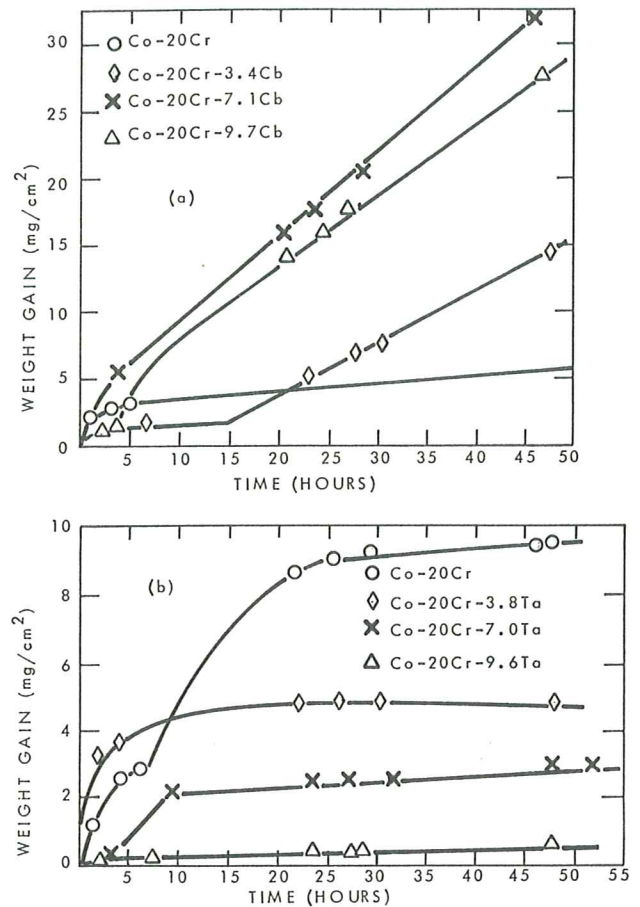

Fig. 17: Comparison of the 1000°C (1830°F) oxidation characteristics of various Co-20% alloys with additions of columbium and tantalum. Tests conducted in flowing oxygen. (a) columbium series (b) tantalum series. After Irving, et al.[51]

In the case of classical "hot corrosion" (Na_2SO_4 fluxing of protective oxide scales with consequent internal attack), the role of retory metals is somewhat less well defined. Beltran[48] generalizes that, to a degree, refractory elements affect hot corrosion resistance in a fashion quite similar to the way in which they affect oxidation resistance. He cites columbium as being quite harmful in Alloy WI-52, but less so in Alloy S-816. Tungsten may be deleterious in HAYNES alloy No. 25, but tantalum is cited as being innocuous in MAR-M 302. Performance of these alloys is compared in Figure 18.

Nagarajan, et al.[53] found that the presence of molybdenum in Co-10% to 25%Cr alloys caused accelerated and sometimes catastrophic hot corrosion for samples tested at 900°C (1650°F) in Na_2SO_4 and NaCl + Na_2SO_4 environments. In Na_2SO_4, addition of 10% molybdenum to 10% to 15% chromium alloys results in catastrophic corrosion caused by classical Na_2SO_4 acidic fluxing. In the higher chromium-content alloys, addition of 10% molybdenum results in catastrophic corrosion as a consequence of the formation of low melting point, volatile oxides of molybdenum which cause extensive scale breakaway. In concurrent work, Nagarajan, et al.[54] report that tantalum additions of up to 10% appear innocuous by contrast. They caution, however, that when sufficient tantalum is present to cause a continuous second-phase network to

develop, extensive penetration attack along phase boundaries will occur.

Richards and Stringer[55] have studied the influence of tungsten, tantalum, and columbium additions to Co-25%Cr alloys upon resistance to corrosion in molten Na_2SO_4 at 900°C (1650°F). They found that the base alloy, Co-25%Cr, exhibited very little attack after a 100-hour immersion in the molten sulfate. In contrast, the addition of 7.5% tungsten caused extremely rapid corrosion to occur in molten Na_2SO_4 at 900°C (1650°F). Replacing the tungsten with 2.5% columbium caused the rate of attack upon the material to be even more rapid, however, replacing tungsten with tantalum at levels up to 8%, however, substantially reduced the rate of attack.

SUMMARY AND CONCLUSIONS

Considerable literature exists which characterizes the role and influence of refractory metals in cobalt-base superalloys. It has been observed that elements such as molybdenum, tungsten, columbium, tantalum, and vanadium play important roles in strengthening of these alloys. They do so by providing solid-solution strengthening, by influencing carbide morphology and precipitation characteristics, and to a lesser
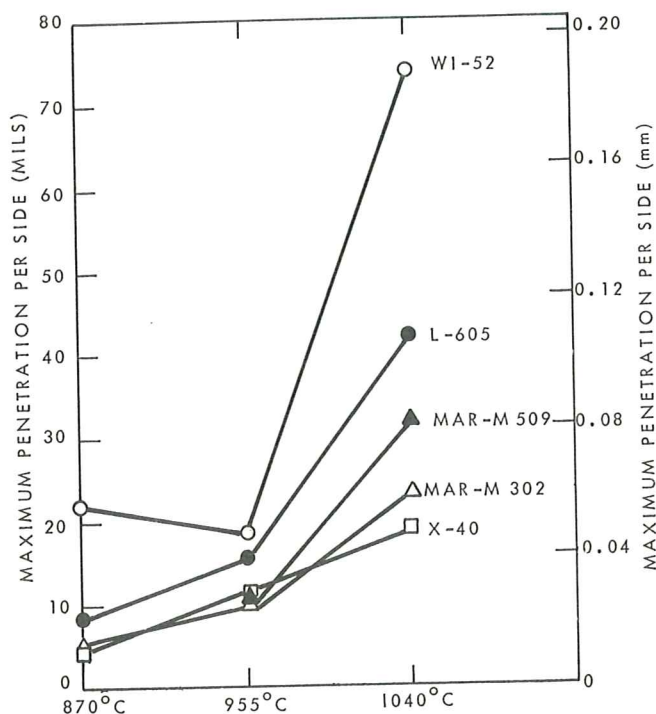

Fig. 18: Relative hot-corrosion resistance of cobalt-base superalloys. After Beltran.[48]

extent by providing for precipitation of intermetallic compounds. Refractory elements exert a strong influence upon the FCC to HCP allotropic phase transformation in cobalt-base alloys and are important in considering stacking-fault related phenomena in these materials.

The observable effects upon various cobalt-base alloy properties, which are at least partially attributable to refractory element content, include improved hardness, high-temperature strength, phase stability, and resistance to various forms of wear. Refractory element additions to cobalt-base alloys are generally less favored for their effect upon environmental properties such as oxidation and hot corrosion. Some are quite deleterious, while other, such as tantalum can be beneficial.

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