

# PRINCIPLES OF ALLOY DESIGN FOR CORROSION AND WEAR SERVICES

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## ABSTRACT

The degradation of materials of construction by corrosion and/or wear is a serious problem for design, engineering, operation, and maintenance personnel in the chemical process industries. As a control measure, the use of high performance, nickel-based and cobalt-based alloys to extend the service life of process equipment is often the most practical and cost-effective solution.

In this paper, the roles of the major alloying elements in these materials are reviewed, in terms of their effects upon resistance to corrosion and wear. In particular, the importance of molybdenum and tungsten in the Ni-Cr-Mo alloys, the effects of silicon in nickel-based alloys, and the effects of chromium and molybdenum in cobalt-based alloys are discussed.

Data relating to field trials and successful applications of many of these alloys are presented in this paper. Industries covered include phosphoric acid production, sulfuric acid processing, and metal finishing.

## INTRODUCTION

Many of today's nickel- and cobalt-based alloys were derived from simple binary and ternary alloys developed between 1905 and 1935. Notable among the early binary alloys were Ni-Cr (patented by A.L.Marsh and E.Haynes), Ni-Mo (patented by A.W.Clement), Ni-Si (patented by A.J.Mandell) and Co-Cr (patented by E.Haynes). With regard to the nickel-based alloys, Ni-Mo was found to be resistant to non-oxidizing media (such as hydrochloric acid), Ni-Cr was found to exhibit passive behavior in oxidizing media such as nitric acid, and Ni-Si was found to resist super-oxidizing media such as chromic acid.

Since the discovery of these binary alloys, the most significant advances, in an alloy design sense, have been:

- a) the combining of these binary alloys to form more versatile Ni-Cr-Mo and Ni-Cr-Si compositions.
- b) the use of some iron in place of nickel, in certain alloys.

- c) the use of copper in certain alloys to improve their resistance to sulfuric and phosphoric acids.
- d) the use of tungsten as a partial substitute for molybdenum to enhance resistance to phosphoric acid and resistance to localized attack in oxidizing, acidic, chloride solutions.

With regard to the Co-Cr binary alloy developed by E.Haynes, this subsequently gave rise to a series of Co-Cr-W and Co-Cr-Mo alloys. At low carbon levels, these alloys were found to be strong over a large temperature range, resistant to many forms of wear, resistant to many aqueous media, and resistant to many hostile, high temperature environments. With deliberate carbon additions, high hardnesses and high resistance to low stress abrasion were attained, although at the expense of ductility and corrosion resistance.

### ALLOY DESIGN

To understand the design philosophies associated with the modern nickel- and cobalt-based alloys, some knowledge of their crystallography is necessary. In the case of the nickel-based alloys, the structural characteristics are relatively simple. In the case of the cobalt-based alloys, the crystallographic characteristics are complex.

Pure nickel exhibits a face centered cubic (fcc) structure throughout the temperature range of the solid state. As regards the solubilities of alloying elements which are vital for corrosion resistance, these are generally high, but are strongly influenced by the presence of minor elements, such as carbon and silicon.

Given that the ideal microstructure for corrosion resistance is single phase (from an electrochemical and compositional homogeneity standpoint), a primary concern of the alloy designer has been to avoid phases other than fcc in the nickel-based corrosion alloys. This has been accomplished not by restricting alloying additions within the soluble range, but by ensuring that the structure is single phase (metastable fcc) upon quenching from a temperature (the solution annealing temperature) at which all additional phases dissolve. In other words, the high temperature structure is maintained to low temperatures by rapid cooling. Subsequent heating to intermediate temperatures (for example, during welding) can result in the precipitation of undesirable (but thermodynamically stable) phases, particularly in the grain boundaries, which constitute ideal nucleation sites. Therefore, the alloy designer is restricted from exceeding the solubility limits too much, and must pay attention to the kinetics of the intermediate temperature, precipitation reactions.

To minimize these precipitation reactions, minor elements such as carbon and silicon are generally held at low levels in the nickel-based wrought alloys. Silicon is a problem, however, in most nickel-based cast alloys, since it is necessary for fluidity. An added problem with castings is elemental segregation (inhomogeneity).

As mentioned, the crystallographic characteristics of the cobalt-based alloys are complex in comparison. This complexity stems from the fact that pure cobalt can exist in two forms. The thermodynamically stable structure at temperatures up to 417°C is hexagonal close packed (hcp); at higher temperatures, it is face centered cubic. Alloying additions serve to stabilize either the hcp or fcc form, by shifting the transformation temperature (up in the case of hcp stabilizers, such as chromium, molybdenum, and tungsten; down in the case of fcc stabilizers, such as nickel, and iron).<sup>1,2</sup>

Upon cooling the cobalt-based alloys from the liquid state, or from the solution annealing temperature, the hcp phase is hard to generate, and the room temperature structure of most cobalt-based alloys is metastable fcc. However, they transform easily when plastically deformed by a mechanism which involves the coalescence of stacking faults, the fcc form of the cobalt-based alloys having a very low stacking fault energy. The resistance to deformation and fracture which result from these characteristics are responsible for the outstanding wear properties of the cobalt-based alloys.

With regard to phases other than fcc and hcp in the cobalt-based alloys, they have been deliberately promoted (in alloys designed primarily for wear), avoided (in alloys for severe corrosion service), or selectively avoided (in the case of high temperature alloys, where some carbide precipitates may be necessary for strength, but intermetallics have a detrimental effect upon ductility).<sup>3</sup>

Given these crystallographic constraints, the task of the alloy designer is to optimize compositions for specific properties. Considering the nickel-based, corrosion-resistant alloys, then the primary concern is the effect of various alloying elements upon the resistance to a particular type of environment, or group of environments.

Generally, chromium enhances the passivity of nickel-based alloys in a wide range of oxidizing media, just as it does in the stainless steels. In fact, there are many similarities between the nickel-based, corrosion-resistant alloys and the austenitic, stainless steels (particularly those with high nickel contents), in terms of the roles of the various alloying elements.

Molybdenum and tungsten increase the resistance of the nickel-based alloys to corrosion in non-oxidizing, acid media. As will be discussed, a specific ratio of molybdenum to tungsten atoms is desirable for resistance to certain media.

With regard to the effects of silicon in the nickel-based alloys, these may be beneficial or detrimental, depending upon the silicon level, the levels of the other alloying elements, and the product form and annealing treatment. As mentioned, high silicon levels promote resistance to super-oxidizing media. This is believed to be related to the development of protective surface films, containing large proportions of silica, in such media, rather than providing passivity in the classical sense.<sup>4</sup>

Even at low levels, however, silicon can be a problem because it promotes the formation of embrittling and sensitizing, intermetallic phases. In castings of the nickel-based alloys, and in high-silicon, nickel-based alloys designed for resistance to super-oxidizing media, strict solution annealing practices are important.

With regard to other possible alloying elements, carbon is usually held as low as possible in the nickel-based alloys (as it is in the austenitic, stainless steels), to avoid sensitization through the formation of grain boundary carbides. The positive effects of copper upon the resistance of nickel-based alloys to phosphoric and sulfuric acids will be discussed in the next section.

Considering now the cobalt-based, corrosion- and wear-resistant alloys, the alloy designer is forced to choose between corrosion resistance and moderate ductility, on the one hand, and low stress abrasion resistance, on the other. For the latter, high carbon contents are necessary, to promote the formation of carbides in the microstructure, during alloy solidification.<sup>5</sup>

In the absence of carbon, the effects of the various alloying elements upon the corrosion resistance of the cobalt-based alloys are similar to those observed in the nickel-based alloys and austenitic, stainless steels. Important points, however, are that solubilities are not necessarily the same (cobalt-based alloys, for example, are more tolerant of minor elements, such as silicon), and that major alloying elements have profound effects on the mechanical properties of the alloys due to their influence on the transformation characteristics.

## MODERN COMPOSITIONS

Several modern, nickel- and cobalt-based compositions are listed in Table 1. The design objectives associated with each of these alloys, some of their properties, and case histories associated with their use are as follows:

### HASTELLOY B-3 Alloy

The B-family of alloys was developed from the Ni-Mo binary for use in strong, non-oxidizing media, such as hydrochloric acid and sulfuric acid (at moderate concentrations). B-3 alloy is a wrought material with reasonable thermal stability. Previous B-family alloys have either been plagued by rapid transformations of the microstructure to  $Ni_4Mo$  or have had their corrosion resistance compromised by alloying additions used to avoid this transformation. The problems associated with this transformation have included cracking during fabrication processes (due to low ductilities) and stress corrosion cracking in service.

The composition of B-3 alloy is such that a different intermetallic,  $Ni_3Mo$ , with slower transformation kinetics, is favored. The chances of intermetallic formation during heating and cooling during annealing or welding are thus reduced considerably.

### HASTELLOY B-42 Alloy

The fact that cast microstructures are less homogeneous than wrought microstructures has been discussed. The micro-cast structures of weldments are also inhomogeneous (segregated). From a corrosion standpoint, this is important since regions lean in a particular element may be prone to higher rates of attack.

B-42 alloy was developed to overcome the problem of higher corrosion rates in the case of B-family weldments. Without the constraints of wrought processing, it is possible to use higher molybdenum levels (42 wt.% in the case of B-42 alloy), such that even the lean weld metal regions equal the wrought products in terms of uniform corrosion rates.

The alloy has been used by a major chemical company in Germany as an overlay, to protect B-family weldments in media containing sulfuric acid.

### HASTELLOY C-22 Alloy

C-22 alloy is based on the ternary Ni-Cr-Mo system with tungsten additions. As such, it is extremely versatile, possessing high resistance to both oxidizing and non-oxidizing acid media. The properties of C-22 alloy are critically dependent upon the relative levels of molybdenum and tungsten. The patent for the alloy, in fact, calls for a Mo:W ratio of between 5:1 and 3:1. Furthermore, it was discovered during development of the alloy that the ratio of  $2 \times \text{Cr:Mo} + (0.5 \times \text{W})$  should fall in the range 2.1 to 3.7 for optimum resistance to a wide range of corrosive media. To illustrate this, a plot of the normalized corrosion rate versus this ratio is presented in Figure 1 for the corrosive medium used in ASTM Standard G 28B (i.e. 23%  $\text{H}_2\text{SO}_4$  + 1.2% HCl + 1%  $\text{FeCl}_3$  + 1%  $\text{CuCl}_2$ , boiling).

With regard to product forms, C-22 alloy was developed primarily for use in the wrought condition. However, due to its high resistance to many corrosive media, it has been used as a weld filler metal for other nickel-based alloys and stainless steels, since weldments of these materials are often prone to preferential attack. It has also been used in weld overlay form to protect critical equipment surfaces.

Two cast versions of C-22 alloy are available, a low-silicon vacuum grade and an air-melting grade with about 0.5 wt% silicon, for enhanced fluidity. As discussed, silicon is detrimental to the corrosion resistance of Ni-Cr-Mo alloys, due to its influence on thermal stability (i.e. the precipitation of secondary, intermetallic precipitates). Therefore, where possible, the vacuum grade is recommended. The effect of silicon content upon the corrosion resistance of C-22 castings in the ASTM G 28A solution (50%  $\text{H}_2\text{SO}_4$  + 42 g/l  $\text{Fe}_2(\text{SO}_4)_3$ , boiling) is shown in Figure 2.

With regard to the industrial uses of C-22 alloy, these have been widespread throughout the chemical processing industries. Two notable successes were for shafts supporting plastic rolls in a hydrochloric etching bath (alloy 400 had failed prematurely in this environment, due

to crevice corrosion) and for evaporators in a sulfuric acid concentrator where alloy 825 had failed due to pitting. The largest order for C-22 alloy to date was for the DRAX flue gas desulfurization system in the U.K. Since its introduction, C-22 alloy has performed well in numerous FGD systems throughout the world.

### HASTELLOY D-205 Alloy

D-205 alloy is a hybrid of the Ni-Cr and Ni-Si binaries. As such, it possesses high resistance to oxidizing and super-oxidizing media. It was designed as an alternate to the high-silicon stainless steels, which are prone to localized attack in the presence of chlorides, and which are easily embrittled during elevated temperature excursions, due to the formation of intermetallics.

The composition of D-205 alloy, which was designed for use in the wrought condition, represents a balance between corrosion performance and processability. Molybdenum was added for improved resistance to localized attack, and copper was found to enhance the resistance of the alloy to moderate concentrations of sulfuric acid.

In evaluating the thermal stability of D-205 alloy, it was discovered that fine precipitates of gamma prime ( $\text{Ni}_3\text{Si}$ ) form in preference to intermetallics of a more embrittling nature. Furthermore, it was discovered that the gamma prime precipitates may be used to strengthen the alloy, in a controlled manner.

Relative to a stainless steel of identical silicon content, D-205 alloy has been shown to be significantly more resistant to sulfuric acid (both reagent grade and commercial grade). This is illustrated in Figure 3, a plot of corrosion rate versus acid concentration, in the range 96 to 99% (commercial).

The primary use of D-205 alloy so far has been in the construction of plate heat exchangers for the sulfuric acid industry. D-205 alloy has allowed the use of these heat exchangers at higher than normal temperatures, thus increasing plant efficiency.

### HASTELLOY G-30 Alloy

G-30 alloy was designed primarily for use in wrought form to resist commercial phosphoric acid. For this environment, a high chromium content, and some copper were found to be optimum, as illustrated in Figure 4, a chart showing the corrosion rates for several commercial alloys. Molybdenum and tungsten were found to play a secondary, but nevertheless important, role, particularly in acids with high chloride contents.

The presence of iron in G-30 alloy is to minimize cost. However the iron content was restricted to 15 wt.% to maintain the superior corrosion performance imparted by the nickel (in particular resistance to stress corrosion cracking and to corrosive attack induced by micro-organisms, e.g., MIC).

The most notable use of G-30 alloy in the phosphoric acid industry has been for heat exchangers, where it has replaced alloys 625 and G-3 (on the basis of lower corrosion rates), and Karbate (on the basis of increased toughness). Currently eleven G-30 heat exchangers are in service.

### ULTIMET Alloy

Among the cobalt-based alloys, Ultimet is unique in that it was designed along the lines of the nickel-based alloys for optimum resistance to a variety of corrosive media. For this reason, the carbon content of the alloy is low (low enough that the wrought, annealed microstructure is free from carbide precipitation), and all the key alloying additions are in the fcc/hcp solid solution.

With regard to the chromium, molybdenum, and tungsten levels, these were selected to provide high resistance to uniform attack in a range of acid media, and high resistance to pitting and crevice attack in chloride-containing media. Surprisingly, molybdenum and tungsten were found to be more effective in cobalt-based alloys (than they are in nickel-based compositions) with regard to their effect on resistance to localized attack. A small addition of nitrogen was found to further enhance the resistance of the alloy to pitting and crevice corrosion.

To attain a balance between the wear properties of Ultimet alloy (which are enhanced by the hcp stabilizers) and other properties, such as processability, fabricability, toughness, and resistance to stress corrosion cracking (all of which are enhanced by fcc stabilizers), nickel and iron were added to the alloy. In fact, the commercial success of the alloy has been strongly influenced by the fact that it is easily (and therefore inexpensively) produced, fabricated into components, and machined. Another major advantage of the alloy, as compared with other wear-resistant, cobalt-based alloys, has been its relatively high weld-metal ductility, which has allowed the application of weld overlay deposits without the risk of cracking.

The higher tolerance of cobalt-based alloys for silicon has not only resulted in the use of the wrought composition in cast form, but also these castings can be used in the as-cast condition, thus avoiding the costs and risks of annealing.

Successful applications of Ultimet alloy to date have included various valve and pump components, cast spray nozzles, and conductor rolls for electrogalvanizing. The conductor rolls are used in the production of galvanized steel for automobiles in the Far East. The corrosion/wear rate of Ultimet alloy in this application is about half that of the previously used Ni-Cr-Mo alloy.

## SUMMARY

Although the compositions of the nickel-based corrosion alloys and cobalt-based corrosion/wear alloys are complex, they are based on sound principles and experience as to the roles of the various alloying elements. In this paper, an insight has been given with regard to these roles, in particular the effects of silicon, chromium, molybdenum and tungsten.

In many situations, the modern compositions described in this paper constitute the most cost-effective materials of construction, especially in light of downtime costs and the costs of hazardous emissions.

## References

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TABLE 1

**Modern Nickel- and Cobalt-Based Compositions (wt.%)**

	Ni	Co	Fe	Cr	Mo	W	Mn	Si	C	Cu	Others
<b>Nickel-Based</b>											
B-3	65	3*	1.5	1.5	28.5	3*	3*	0.1*	0.01*	0.2*	-
B-42	58	-	-	-	42	-	-	-	-	-	-
C-22	56	2.5*	3	22	13	3	0.5*	0.08*	0.01*	-	V-0.35*
D-205	65	-	6	20	2.5	-	-	5	0.03*	2	-
G-30	43	2*	15	30	5.5	2.5	1.5*	1*	0.03*	2*	Cb-0.8
<b>Cobalt-Based</b>											
ULTIMET	9	54	3	26	5	2	0.8	0.3	0.06	-	N-0.08

\* Maximum

Figure 1  
Effect of 2Cr:Mo+W/2

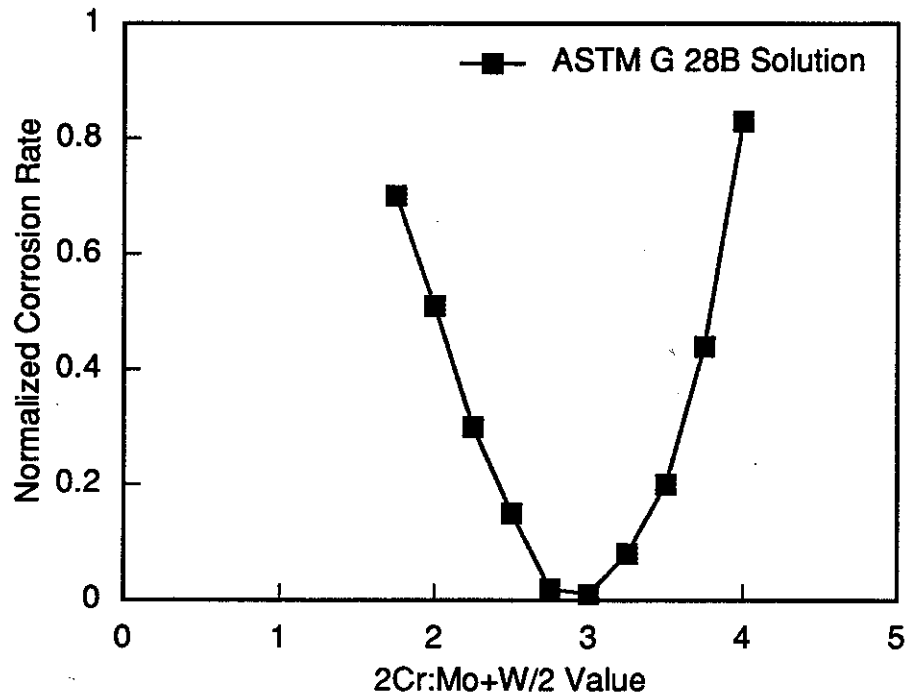


Figure 2  
Effect of Si Content in Cast C-22

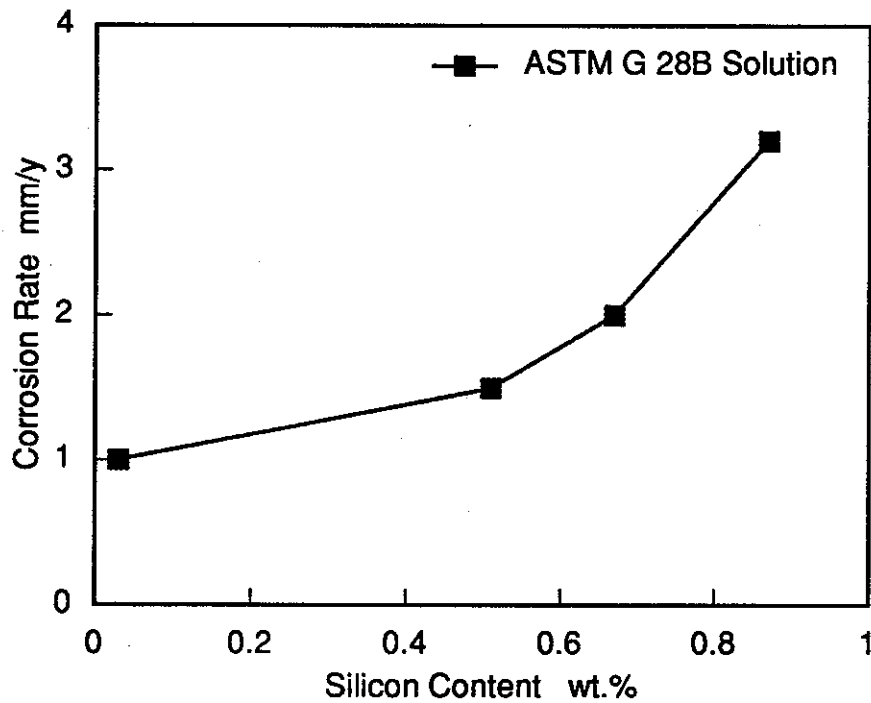


Figure 3  
Data for Sulfuric Acid at 130°C

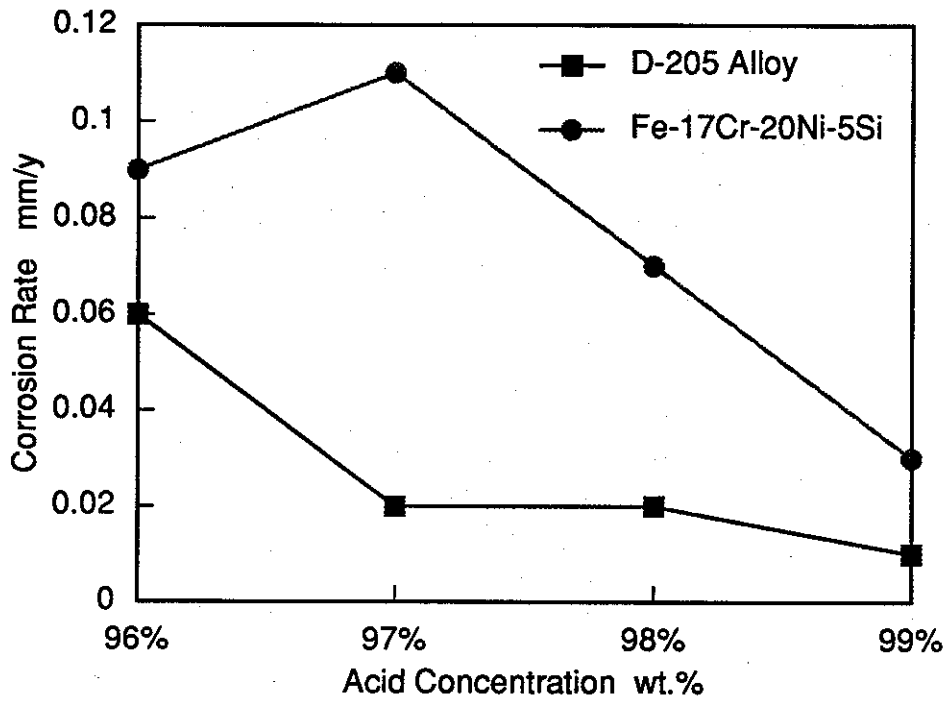


Figure 4  
Effect of Cr & Cu in Phosphoric Acid

