

## Metallurgy

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### Metallurgical Primer

Before discussing the metallurgy of the nickel and cobalt alloys, it is important that certain metallurgical terms are understood. First and foremost, it should be understood that an *alloy* is a mixture of metals, possibly containing small quantities of non-metals, such as carbon. The predominant metal in the alloy is known as the *base*.

A *solid solution* is an alloy in the solid state having a single atomic structure or *phase*. *Second phases* are possible when the combined levels of alloying additions to the base exceed their solubility limits. So, as with a liquid solution, there are natural limits to how much can be dissolved in a metallic material of a given atomic structure, and as with a liquid solution, the higher the temperature, the more can be dissolved. Fortunately, it is possible to create supersaturated solid solutions by heat treating materials at high temperatures where the solubilities are higher, then rapidly cooling the materials to room temperature, or at least below 500°C, where the diffusion of atoms (the main catalyst for microstructural change) is no longer appreciable. Holding alloys at high temperatures, to dissolve unwanted second phases in their microstructures, is known as *solution annealing*. Rapid cooling, to lock in the high temperature microstructure, is known as *quenching*, and is best performed in cool water.

The problem with such supersaturated materials is that they are prone to second phase *precipitation* during excursions above 500°C, when diffusion becomes appreciable. Such excursions are common during welding, for example.

Unfortunately, precipitates tend to nucleate and grow at microstructural imperfections, such as grain boundaries. These then become prone to preferential corrosion attack.

Not all second phase precipitates are detrimental. Those that precipitate homogeneously (i.e. throughout the microstructure, rather than just at the grain boundaries) can be used to strengthen materials. This is known as *precipitation-hardening* or *age-hardening*. The heat treatments used to induce such precipitates often involve multiple steps in the temperature range 500°C to 800°C.

The microstructures of wrought and cast alloys comprise numerous *grains*, within which the crystal structure is aligned in a certain direction. However, these grains can sub-divide under the action of mechanical stress or temperature by a process known as *twinning*, whereby bands of material within a grain can realign.

*Grain boundaries* (of irregular geometry) and *twin boundaries* (which are straight and parallel) are very important microstructural features, since they are preferred nucleation sites for second phase precipitates.

The *major* alloying elements determine the general behavior of a material. However, *minor* alloying elements are also important. Some minor elements are there to ensure successful melting and processing; some are used to fine-tune performance in specific environments. Others are added to induce hardening precipitates.

Except in the case of the few precipitation-hardenable nickel alloys designed to resist aqueous corrosion, strengths are determined largely by the major alloying elements. These provide solid solution strengthening. Large atoms such as molybdenum are particularly effective strengtheners.

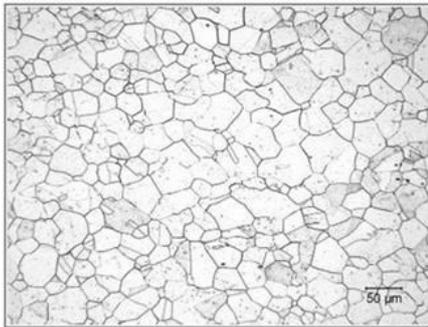
To maximize the corrosion resistance of the nickel alloys, many are deliberately overalloyed and reliant upon the previously mentioned process of solution annealing and quenching to optimize their microstructures. Even those that are not overalloyed are prone to second phases, due to the presence of insoluble residuals, such as carbon.

### **Nickel Alloy Metallurgy**

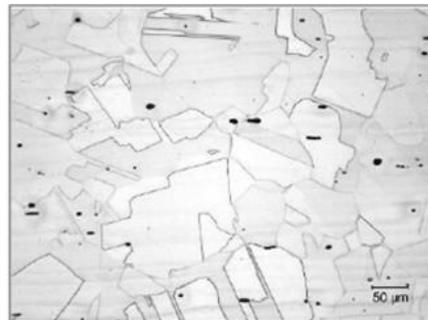
The purpose of this part of the manual is to provide information on the physical metallurgy of the four groups of wrought, corrosion-resistant, nickel alloy with which Haynes International is associated (i.e. the Ni-Cr, Ni-Mo, Ni-Cr-Mo, and Ni-Cr-Fe groups). For completeness, however, microstructures of materials from the other three groups will be shown and commented upon.

As already discussed, the atomic structure of pure nickel is face-centered cubic (FCC), otherwise known as gamma phase within the realm of nickel alloy metallurgy. Commercially-pure nickel (Ni), of which there are several grades, and the nickel-copper (Ni-Cu) alloys generally exhibit stable FCC microstructures, although (due to the insolubility of impurity carbon in wrought products from these two groups), carbides, or even free carbon, can be observed in grain boundaries or dispersed throughout these materials. The presence of carbides is evident in the following microstructures of annealed sheets of Nickel 200 and MONEL<sup>®</sup> alloy 400:

**Microstructure of Ni-200 Sheet (with evidence of grain boundary carbide precipitation)**



**Microstructure of MONEL<sup>®</sup> alloy 400 sheet (with evidence of free carbon dispersoids)**



Incidentally, unless otherwise stated, the optical photomicrographs exhibited in this manual involved the following metallographic procedures:

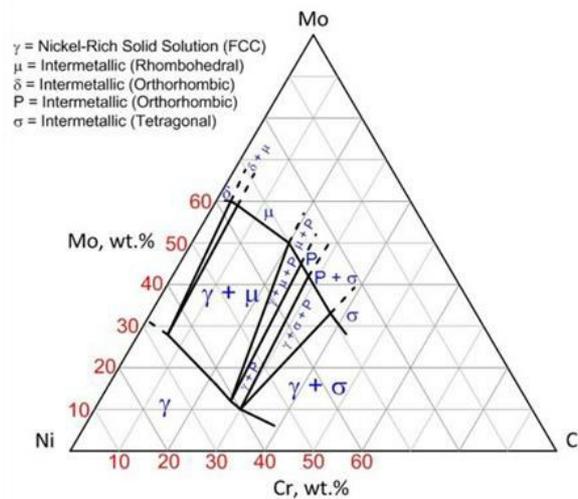
- . Polish the mounted sample to 0.5 mm alumina.
- . Swab with cotton under running water.
- . While still wet, immerse in a solution of 95 ml of reagent grade (37 wt.%) hydrochloric acid + 5 g oxalic acid (added in crystalline form).
- . Electrolytically etch at 5 V, making the sample the anode.
- . Break contact upon visually detecting a change in reflectivity.
- . Agitate sample vigorously in etchant, to remove superfluous film.
- . Remove under running water.
- . Clean with methanol.
- . Dry under hot air.

This etchant is known as the “All Purpose Etch” at Haynes International.

It is appropriate to combine the discussions of alloys from the Ni-Cr and Ni-Cr-Mo groups, since some of the commercially-important, wrought, corrosion-resistant Ni-Cr alloys contain significant levels of molybdenum, so that the same phase diagrams are relevant.

The 850°C section of the Ni-Cr-Mo phase diagram, shown below, provides some indication of the solubilities of chromium and molybdenum in nickel, in the absence of other alloying elements. It indicates that, at this temperature, and with a chromium content of 30 wt.%, then the molybdenum content must be less than 10 wt.%, to maintain a single-phase (FCC) structure. Conversely, if the molybdenum content is 25 wt.%, then the chromium content should be less than 10 wt.%.

**850°C Section of the Ni-Cr-Mo Ternary System (Raghavan et al, 1984)**



Several Ni-Cr and Ni-Cr-Mo materials (for example HASTELLOY® C-4, C-22HS®, HYBRID-BC1®, Alloy 59, and G-35® alloys) are effectively ternary systems. All except C-4 alloy (which is well within the gamma phase field, and consequently relatively stable) are close to the gamma phase field boundary. This is due to a trend whereby designers of such materials have chosen to maximize the contents of chromium and molybdenum, for enhanced corrosion resistance, while using solution annealing and quenching to maintain an (albeit meta-stable) single-phase (FCC) microstructure.

Such an approach is limited by the need to avoid continuous precipitation of second phases (such as  $\mu$  phase) in the grain boundaries during subsequent thermal cycles (for example, during welding).

To complicate matters, other second phases are possible in the Ni-Cr and Ni-Cr-Mo alloys. They can occur at temperature ranges below or (less likely) above 850°C. They can result from the presence of residual elements (notably carbon). Alternatively, they can be triggered by other alloying additions.

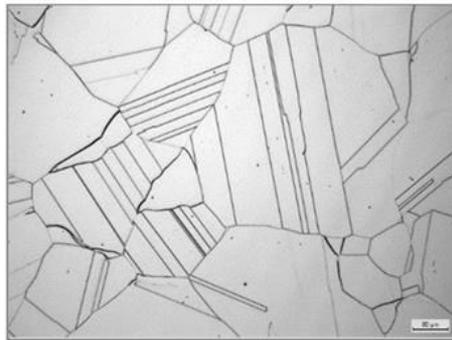
With regard to second phases associated with different temperatures, an ordered phase of the type A2B, or in this case  $Ni_2(Cr, Mo)$ , can occur in the range 300°C to 650°C by long-range ordering (Raghavan et al, 1982). The driving force for this ordering reaction depends upon the atomic ratios of the various alloying elements. The precipitation reaction is homogeneous, with no preferential precipitation at the grain boundaries or twin boundaries. At low temperatures within the range, the reaction is impeded by low diffusion rates; however, at temperatures closer

to 650°C, the reaction can be strong enough to be used as a strengthening process (*Pike et al, 2003*). Indeed, this is the reaction used to strengthen C-22HS<sup>®</sup> alloy.

The most important second phase resulting from residual (unwanted) elements is M<sub>6</sub>C carbide, which is prevalent in the high-molybdenum alloys, even at very low residual carbon levels (0.005 wt.% or less). *Hodge, 1973* indicates that M<sub>6</sub>C forms in the temperature range 650°C to 1038°C in C-276 alloy (as compared with a range of 760°C to 1093°C for μ phase). The same reference indicates that the kinetics of carbide formation are faster than those of m phase.

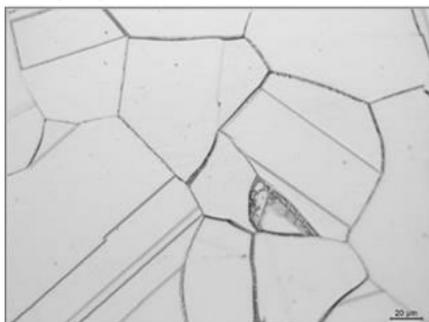
The microstructure of G-35<sup>®</sup> alloy, a representative of the Ni-Cr group (containing 33.2 wt.% chromium and 8.1 wt.% molybdenum) is shown in the following figure. It is generally free of second phase precipitates, although some are evident in selected grain boundaries. These are likely carbide precipitates, since the maximum carbon content in G-35<sup>®</sup> alloy is high (0.05 wt.%), relative to the wrought Ni-Cr-Mo alloys, for which the maximum carbon content is typically 0.01 wt.%.

#### Microstructure of Mill Annealed G-35<sup>®</sup> Sheet

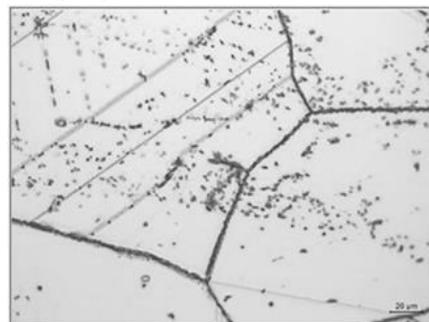


To evaluate the propensity for second phase precipitation (i.e. thermal stability) in alloys of this kind, it is usual to subject them to long-term aging treatments, at different elevated temperatures (normally above 500°C, where diffusion of elements becomes appreciable). Such temperatures are well beyond the use temperatures of the corrosion-resistant nickel alloys, and the exposure times infinitely higher than those experienced during welding; nevertheless, they provide a glimpse of the “true” stability of the material. Below are microstructures (photographed using an optical microscope) of G-35<sup>®</sup> alloy, after aging for 8,000 hours at 538°C (1000°F), 649°C (1200°F), and 760°C (1400°F). Higher magnification, secondary electron images of the samples aged at 649°C and 760°C, taken on a scanning electron microscope, are also shown (*Srivastava and Crook, 2016*).

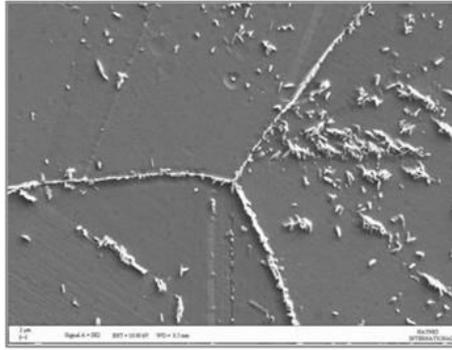
#### Microstructure of Mill Annealed G-35<sup>®</sup> Sheet After Aging for 8000 h at 538°C (1000°F)



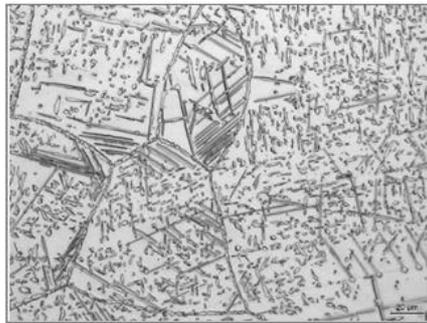
#### Microstructure of Mill Annealed G-35<sup>®</sup> Sheet After Aging for 8000 h at 649°C (1200°F)



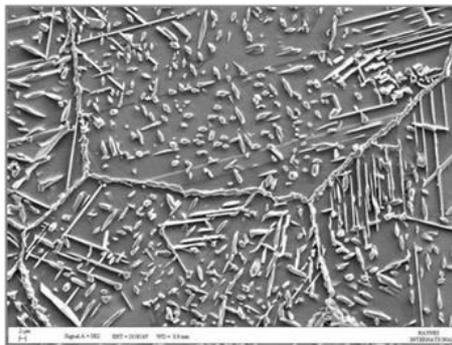
**Secondary Electron Image of Mill Annealed G-35<sup>®</sup> Sheet After Aging for 8000 h at 649°C (1200°F)**



**Microstructure of Mill Annealed G-35<sup>®</sup> Sheet After Aging for 8000 h at 760°C (1400°F)**



**Secondary Electron Image of Mill Annealed G-35<sup>®</sup> Sheet After Aging for 8000 h at 760°C (1400°F)**



The optical photomicrograph of the microstructure after aging at 538°C indicates some second phase precipitation in the grain boundaries. The optical photomicrograph and secondary electron image of G-35<sup>®</sup> alloy aged at 649°C indicate more extensive grain boundary precipitation, together with some intra-granular, second phase precipitates. After long-term aging at 760°C, the alloy exhibits a large amount of inter- and intra-granular precipitation, and notably an array of acicular particles within the grains.

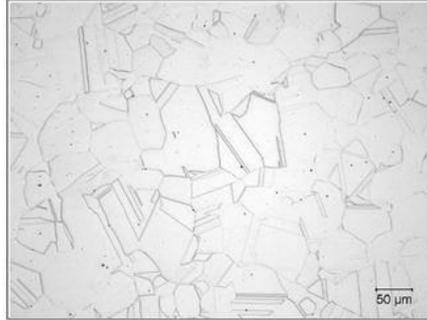
Energy-dispersive X-ray (EDX) analyses revealed that the second phases present in G-35<sup>®</sup> alloy, after long-term exposure at 649°C and 760°C, are:

- . A chromium-rich (about 90 wt.%), nickel-free phase (presumed to be alpha-chromium).
- . A phase containing about 45 wt.% chromium, 30 wt.% nickel, and 23 wt.% molybdenum.
- . Four phases containing various levels of carbon (1, 3, 6, and 11 wt.%), with varying levels of other elements.

The annealed microstructure of HASTELLOY<sup>®</sup> C-276 alloy is shown in the optical photomicrograph below. It features “clean” (i.e. precipitate-free, or undecorated) grain

boundaries, and, like G-35<sup>®</sup> alloy, annealing twins. The small, black particles dispersed throughout the microstructure are most likely oxide impurities. Although photographs of long-term aged microstructures are unavailable for C-276 alloy, it is known that  $\sigma$  phase and carbides occur in C-276, as already discussed.

#### **Microstructure of Mill Annealed C-276 Sheet**



Most of the Ni-Cr-Mo materials are microstructurally similar to C-276 alloy. However, whereas