Heat Treatment

Heat Treatment

Recommended Procedures and Temperatures Applicable to:
Corrosion-resistant Alloys
High-temperature Alloys
Wear & Corrosion-resistant Alloy

The heat treatment of the HAYNES® and HASTELLOY® alloys is a very important topic. In the production of these wrought materials, there are many hot- and cold-reduction steps, between which intermediate heat treatments are necessary, to restore the optimum properties, in particular ductility. In the case of the corrosion-resistant alloys, these intermediate heat treatments are generally solution-annealing treatments. In the case of the high-temperature alloys, this is not necessarily so.

Once the materials have reached their final sizes, they are given a final anneal. This is usually a solution-anneal; however, a few high-temperature alloys (HTA) are final annealed at an adjusted temperature, to control grain size, or some other microstructural feature.

Subsequent fabrication of these as-supplied materials can again involve hot- or cold-working, as discussed in the Hot-working and Cold-working sections of this guide. Again, working often involves steps, with intermediate annealing (normally solution-annealing for the CRA materials) treatments to restore ductility. Beyond that, fabricated components will require a final anneal (normally a solution-anneal for the CRA materials), to restore optimum properties prior to use, or (in the case of the age-hardenable alloys) to prepare them for age-hardening.

Applicable to:
Corrosion-resistant Alloys

The compositions of the corrosion-resistant alloys (CRA) comprise a nickel base, substantial additions of chromium and/or molybdenum (in some cases partially replaced by tungsten), small additions such as copper (to enhance resistance to certain media) and iron (to allow the use of less expensive raw materials), and minor additions such as aluminum and manganese, which help remove deleterious elements such as oxygen and sulfur, during melting. As-supplied, they generally exhibit single phase (face-centered cubic, or gamma) wrought microstructures.

In most cases, the presence of a single phase microstructure in as-supplied (CRA) materials is due to a high temperature, solution-annealing treatment, followed by quenching (rapid cooling), to “lock-in” the high-temperature structure. Left to cool slowly, most of these alloys would contain second phases (albeit in small amounts), commonly within the structural grain boundaries, as a result of the fact that the combined contents of the alloying additions exceed their solubility limits.

This is exacerbated by the fact that, despite sophisticated melting techniques and procedures, traces of unwanted elements (with very low solubility), such as carbon and silicon, can be present. Fortunately, solution-annealing, followed by quenching (by water or cold gas), solves this problem also.

The corrosion-resistant alloys are usually supplied in the solution-annealed condition, and their normal solution-annealing temperatures are given in the table below. They represent temperatures at which phases other than gamma (and, in rare cases, primary carbides and/or nitrides) dissolve, yet provide grain sizes within the range known to impart good mechanical properties. Primary carbides and/or nitrides are seen in C-4 alloy, due to the presence of titanium.

In the case of the corrosion-resistant alloys (CRA), the terms solution-annealed and mill-annealed (MA) are generally synonymous; however, the temperatures used in continuous hydrogen-annealing furnaces (in sheet production) are adjusted to compensate for the line speeds (hence time at temperature).

Solution-annealing Temperatures of the Corrosion-resistant Alloys (CRA)

Alloy	Solution-annealing Temperature*		Type of Quench
	°F	°C	-
B-3®	1950	1066	WQ or RAC
C-4	1950	1066	WQ or RAC
C-22®	2050	1121	WQ or RAC
C-22HS®	1975	1079	WQ or RAC
C-276	2050	1121	WQ or RAC
C-2000®	2100	1149	WQ or RAC
G-30®	2150	1177	WQ or RAC
G-35®	2050	1121	WQ or RAC
HYBRID-BC1®	2100	1149	WQ or RAC

*Plus or Minus 25°F (14°C)
WQ = Water Quench (Preferred); RAC = Rapid Air Cool

There are no specific rules regarding the times required to heat up, then anneal, the corrosion-resistant alloys (CRA), since there are many types of furnace, involving different modes of loading, unloading, and operation. There are only general guidelines.

The temperature of the work-piece being annealed should be measured with an attached thermocouple, and recording of the annealing time should begin only when the entire section of the work-piece has reached the recommended annealing temperature. It should be remembered that the center of the section takes longer to reach the annealing temperature than the surface.

The general guidelines regarding time are:

- Normally, once the whole of the workpiece is at the annealing temperature, the annealing time should be between 10 and 30 minutes, depending upon the section thickness.
- The shorter times within this range should be used for thin sheet components.
- The longer times should be used for thick (heavier) sections.

Rapid cooling is essential after annealing, to prevent the nucleation and growth of deleterious second phase precipitates in the microstructure, particularly at the grain boundaries. Water quenching is preferred, and highly recommended for materials thicker than 3/8 in (9.5 mm). Rapid air cooling has been used for thin sections. The time between removal from the furnace and the start of quenching must be as short as possible (and certainly less than three minutes).

Special precautions are necessary with B-3® alloy. Although more stable than other nickel-molybdenum alloys (particularly its predecessor, B-2® alloy), it is still prone to significant, deleterious, microstructural changes in the temperature range 1100-1500°F (593-816°C), especially after being cold-worked. Thus, care must be taken to avoid exposing B-3® alloy to temperatures within this range for any length of time. B-3® alloy should be annealed in furnaces pre-heated to the annealing temperature (1950°F/1066°C), and with sufficient thermal capacity to ensure rapid recovery of the temperature after loading of the furnace with the B-3® work-piece.

One of the potential problems associated with these microstructural changes (which can occur during heating to the annealing temperature) in the nickel-molybdenum (B-type) alloys is cracking due to residual stresses, in cold-worked material. Shot peening of the knuckle radius and straight flange regions of cold-formed heads, to lower residual tensile stress patterns, has been found to be very beneficial in avoidance of such problems.

Applicable To:
High-temperature Alloys

The high-temperature alloys (HTA), whether based on nickel, cobalt, or a mixture of nickel, cobalt, and iron, are compositionally much more complicated. However, as in the CRA alloys, chromium is an important alloying element, enabling the formation of protective, surface films (particularly oxides) in hot gases.

Large atoms such as molybdenum and tungsten are used to provide solid-solution strength to many of the high-temperature alloys. Those relying on age-hardening for strength include significant quantities of elements such as aluminum, titanium, and niobium (columbium), which can form extremely fine precipitates of second phases (“gamma prime” and “gamma double prime”) known to be very effective strengtheners.

Aluminum can play another role in the high temperature alloys, and that is to modify the protective films (oxides, in particular) that form on the surfaces of these materials at high-temperatures, in the presence of oxygen, etc. Indeed, aluminum oxide is very adherent, stable, and protective.

Unlike the CRA materials, in which carbon is generally a negative actor, the high-temperature HAYNES® and HASTELLOY® (HTA) alloys rely upon deliberate carbon additions, or rather the carbides they induce in the microstructures, to provide the necessary levels of strength (particularly creep strength) for high-temperature service. In some cases, these carbides form during solidification of the materials (primary carbides). In other cases, they form during high-temperature exposure, in the solid state (secondary carbides).

As a consequence of the need for specific carbide types and morphologies in the HTA materials, annealing is a much more complicated subject, especially between steps in the manufacturing and fabrication processes.

The high-temperature HAYNES® and HASTELLOY® alloys are normally supplied in the solution-annealed condition, which is attained by heat treatment at the following temperatures (or within the specified ranges):

Solution-annealing Temperatures of the High-temperature Alloys (HTA)

Alloy	Solution-annealing Temperature/Range		Type of Quench
	°F	°C	-
25	2150-2250	1177-1232	WQ or RAC
75	1925*	1052*	WQ or RAC
188	2125-2175	1163-1191	WQ or RAC
214®	2000	1093	WQ or RAC
230®	2125-2275	1163-1246	WQ or RAC
242®	1900-2050	1038-1121	WQ or RAC
244®	2000-2100	1093-1149	WQ or RAC
263	2100 ± 25	1149 ± 14	WQ or RAC
282®	2050-2100	1121-1149	WQ or RAC
556®	2125-2175	1163-1191	WQ or RAC
625	2000-2200	1093-1204	WQ or RAC
718	1700-1850**	927-1010**	WQ or RAC
HR-120®	2150-2250	1177-1232	WQ or RAC
HR-160®	2025-2075	1107-1135	WQ or RAC
HR-224®			WQ or RAC
HR-235®	2075-2125	1135-1163	WQ or RAC
MULTIMET®	2150	1177	WQ or RAC
N	2150	1177	WQ or RAC
R-41	2050	1121	WQ or RAC
S	1925-2075	1052-1135	WQ or RAC
W	2165	1185	WQ or RAC
WASPALOY	1975	1079	WQ or RAC
X	2125-2175	1163-1191	WQ or RAC
X-750	1900*	1038*	WQ or RAC

WQ = Water Quench (Preferred); RAC = Rapid Air Cool
*Bright (Hydrogen) Annealing Temperature
**Not Strictly a Solution-annealing Temperature Range (More a Preparatory Annealing Temperature Range)

In the solution-annealed condition, the microstructures of the high-temperature alloys (HTA) generally consist of primary carbides dispersed in a gamma phase (face-centered cubic) matrix, with essentially clean (precipitate-free) grain boundaries. For the solid-solution strengthened alloys, this is usually the optimum condition for both high-temperature service, and for room temperature fabricability.

Although the HAYNES® and HASTELLOY® alloys should not be subjected to stress relief treatments at the sort of temperatures used for the steels and stainless steels, for fear of causing the precipitation of undesirable second phases (particularly in the alloy grain boundaries), some lower annealing temperatures have been used for the high-temperature alloys

(HTA) between processing steps, to restore the ductility of partially-fabricated workpieces. These so-called intermediate annealing temperatures should be used with caution, since they too are likely to result in the aforementioned grain boundary precipitation. Some minimum, intermediate annealing temperatures are given in the following table (for selected solid-solution strengthened HTA materials):

Minimum Intermediate Annealing Temperatures (HTA)

Alloy	Minimum Intermediate Annealing Temperature	
	°F	°C
25	2050	1121
188	2050	1121
230®	2050	1121
556®	1900	1038
625	1700	927
HR-120®	1950	1066
HR-160®	1950	1066
S	1750	954
X	1850	1010

Whether an intermediate annealing temperature (rather than a solution-annealing temperature) is appropriate between processing steps will depend upon the alloy and the effects of the lower temperature upon microstructure, and upon the nature of the subsequent operation. These issues must be studied carefully, and advice sought.

Annealing During Cold (or Warm) Forming

Applicable To:
High-temperature Alloys

The response of the HAYNES® and HASTELLOY® high-temperature alloys (HTA) to heat treatment is very dependent upon the condition of the material prior to the treatment. When the material is not in a cold- or warm-worked condition, the principal response is usually a change in the amount and morphology of the secondary carbide phases. Other minor effects might occur, but the grain structure normally remains the same (in the absence of prior cold or warm work).

When these alloys have been subjected to cold- or warm-work, the application of a solution or intermediate anneal will almost always alter the grain structure. Moreover, the amount of prior cold- or warm-work will significantly affect the grain structure, and consequently the mechanical properties of the material.

The following table indicates the effects of heat-treatments (of 5 minutes duration) at various temperatures upon the grain sizes of sheets of several high temperature alloys, subjected to different levels of cold-work.

Effects of Cold-work and Heat Treatment Temperature on Grain Size

Cold-work	Heat Treatment Temperature	ASTM Grain Size Produced

%	°F	°C	25	230®	556®	X
0	None		3.5-4	5-6	5-6	4-5
10	1850	1010	NA	NA	NR	NR
	1950	1066	NR	NR	NR	NR
	2050	1121	NR	NFR	5-5.5	5-7
	2150	1177	4-4.5	4-7	5-5.5	NA
	2250	1232	3-4.5	6.5-7	NA	NA
15	1950	1066	7	NA	NA	NA
	2050	1121	6-7	NA	NA	NA
	2150	1177	5-7	NA	NA	NA
	2250	1232	3-4.5	NA	NA	NA
	1850	1010	NA	NA	NR	NFR