## Technical Data Sheet

Bright Annealing

Annealing is a critical production step. If performed poorly, metal surfaces can be rendered stained, pitted, or cracked, and the metal susceptible to corrosion. Corrosion damage may be revealed in a number of ways, from stress corrosion cracking to intergranular attack or general corrosion. Any number of contaminants left on the tubing surface can and will cause damage during heat treatment. This article attempts to address a number of misconceptions that exist about annealing and bright annealing, in particular. Sensitization and carbide stabilizing anneals are also addressed.

For **bright annealing** to be effective, tube surfaces must be clean and free of foreign matter. The annealing atmosphere must be relatively free of oxygen (if a bright result is desired). This is accomplished by removing nearly all gas (creating a vacuum) or by displacement of oxygen and nitrogen with dry hydrogen or argon. For common stainless steel alloys, the minimum atmosphere quality required is about -40°F (-40°C) on a dew point scale (for hydrogen or argon atmosphere) or less than 10^{-1} Torr partial pressure of water (for vacuum annealing).

Oxygen concentrations are critical whether measured in terms of dew point, which is the custom for annealing in hydrogen or argon atmospheres, or as measured on a partial pressure scale, which is the custom for vacuum annealing. Austenitic stainless tubing in such an atmosphere can be heated to above 1900°F (1038°C) to dissolve carbides and relieve residual stresses. In such an atmosphere at peak temperature, oxides will be minimal. Best results can be obtained by heating as rapidly as feasible. Slow heating will result in oxidation at intermediate temperatures. Higher peak temperatures produce a more reducing condition and a brighter final appearance.
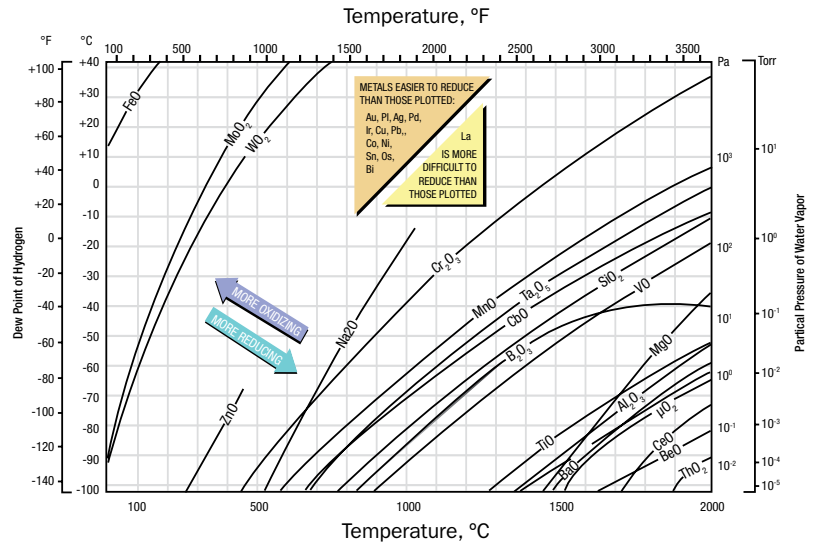
Furnace soak time is not particularly critical for stainless solution annealing. An old rule of thumb for soak time is an hour per inch of section thickness. Using this as a guide, 0.065 inch thick tubing should soak for 4 minutes at temperature. Fast cooling is critical for corrosion resistance; slow cooling can result in sensitization and diminished corrosion resistance. Slow cooling also subjects the product to a more oxidizing condition (generally not desirable).

The metallurgy of bright annealing has been reasonably well defined for some time. In order to achieve a bright result, the most stable oxide forming element in an alloy in any significant concentration must be reduced at peak temperature and atmosphere quality rather than oxidized. For the common austenitic stainless alloys such as 304L and 316L, the most stable oxide former present in significant concentrations is chromium. As such the oxidation potential of chromium at peak annealing temperatures and atmosphere quality

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will largely determine whether the stainless will be bright. The previous figure is a Metal – Metal Oxide Equilibria diagram in pure hydrogen atmospheres.[1] The lines on this diagram show where the oxidation reaction is approximately equal to the reducing reaction. To get a 'bright' result you will need to be a little hotter and/or better in atmosphere quality. If an atmosphere condition exists which is below and/or to the right of an equilibrium line of relevance, the condition is a reducing one, where little oxide should exist on the surface. When the opposite condition exists for chromium, oxidation of chromium will be favored. From this diagram it can be seen that in order to reduce Cr_2O_3, temperatures higher than 1850°F (1010°C) are needed at a dew point of -40°F or lower. Please note that this diagram also explains nicely why slow heating or cooling is undesirable if a bright surface finish is desired.

Well-maintained industrial hydrogen or argon furnaces can typically achieve operating dew point levels in the range of -40 to -50°C (-40 to -58°F). It should be noted that depending on the alloys being annealed, this quality level may or may not be necessary. Typically, hydrogen or argon can be throttled to some extent to achieve the quality of atmosphere required.

However, alloys which contain high levels of stable oxide formers such as aluminum, titanium and, to a lesser extent, columbium, will always be somewhat oxidized in spite of good bright annealing practices. Modern industrial equipment cannot achieve the levels of atmospheric quality needed to prevent oxidation of these elements.

When a truly bright-annealed surface is required even with these alloys (brazing for example) special techniques are used. These include using a very thin nickel plating (easily reduced barrier to oxidation), pre-pickling in strong reducing acids to deplete these elements from a thin surface layer, and, lastly, using activated ion (deadly fluorine gas) annealing.

There are some operational differences between using **argon** or **hydrogen** gas. First, hydrogen and oxygen are an explosive mixture over a wide concentration range. Ignition can occur very easily. Hydrogen is thermally far more conductive than argon, which is used as an insulating gas between glass windowpanes. This means that

heating and cooling times are less when using hydrogen, and that the energy consumption will be significantly higher (cuts insulating efficiency). High velocity furnace gas should be used for fast cooling immediately following any required soak time. This gas is typically recirculated at high velocity through a heat exchanger to remove heat.

Vacuum furnaces can generally achieve the best atmospheric quality for bright annealing purposes. Vacuum levels better than 1×10^{-3} Torr should be possible in well-maintained industrial equipment. The disadvantages of vacuum annealing are long heating times, long soak through times (long cycle times), increased maintenance of the equipment, and difficult cooling. Fast cooling is generally achieved by back filling the chamber with argon or nitrogen and then recirculating this gas at high velocity through a heat exchanger to remove heat. Quench times should be adequate for common 304L and 316L. Less stable alloys such as duplex 2205 or 2507 may not be compatible or may require special handling for best corrosion resistance.

Sensitization occurs when chromium or molybdenum carbides precipitate, typically during field welding or during service in the temperature range of 900–1500°F (480–814°C). When this occurs, chromium and molybdenum are no longer available to protect the alloy in corrosive environments and the metal is "sensitized". Sensitized alloys will be more susceptible to various types of corrosion such as intergranular SCC (stress corrosion cracking) and pitting.

One approach for avoiding sensitizations is to lower the carbon level as in the "L" grades such as 304L and 316L. This reduces the driving force for carbide precipitation, slowing precipitation. Please see the figure next page.

Data shown is typical, and should not be construed as limiting or necessarily suitable for design. Actual data may vary from those shown herein.

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Stabilizing Anneals

Some alloys such as 321 stainless, alloys 20 and 825 are designed to achieve optimum sensitization resistance when first solution annealed then followed by a relatively low temperature stabilizing anneal.

Sensitization is prevented in titanium or columbium-containing alloys through the use of a relatively low temperature anneal that ties up carbon by precipitating titanium or columbium carbides preferentially to chromium or molybdenum. This leaves chromium and molybdenum in solution and available for resisting corrosive environments. Typically, this type of annealing is performed at 1550–1800°F (845-980°C) depending on the specific alloy. Because of what this low temperature anneal accomplishes, it is more correctly a stabilization treatment than a solution anneal.

RathGibson uses only bright annealing in our standard production but can perform stabilizing anneals on request. However, for chromium-containing alloys such as 825, a low temperature anneal (1725–1800°F) (940–982°C) will result in a dark colored product due to formation of some chromium oxides. Industrial furnaces develop atmosphere dew point (quality) levels such that temperatures much lower than 1900°F will result in some visual chromium oxide formation. The color obtained is a function of alloy, atmosphere quality and temperature. If these variables are all essentially fixed, little can be done about the resultant color. If OD appearance or the presence of oxide is critical for other reasons, RathGibson can OD-polish. Our sales group can develop cost estimates if you have interest.
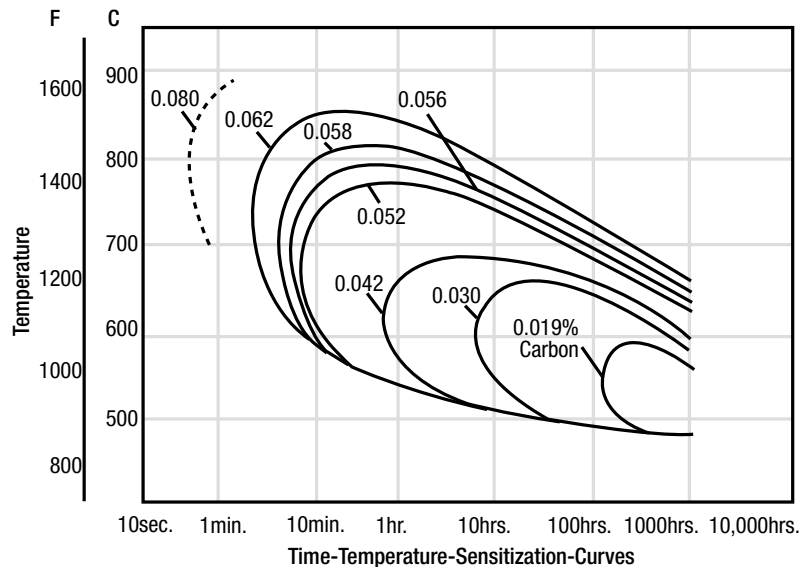

Time required for formation of carbide precipitation in stainless steels with various carbon contents. Carbide precipitation forms in the areas to the right of the various carbon-content curves. Within time periods applicable to welding, chromium-nickel stainless steels with 0.05% carbon would be quite free from grain boundary precipitation.

Soak times for stabilizing anneals are frequently limited for long products such as tubing. This is simply because such long products are typically annealed in continuous roller hearth furnaces which have a minimum speed and cannot be fully stopped. Tubing is rolled into the furnaces, heated to temperature and rolls out the other end. The soak time is limited by the minimum furnace speed and its length. Stabilizing treatments for plate are typically specified as one hour at temperature minimum. Unfortunately, this may be impossible in continuous furnaces.

Stress-Relief Annealing

ASTM A249 Supplemental Requirement 1 (S1) specifies a 1550–1650°F (845-900°C) stress-relief anneal after "roll straightening" followed by air or slow cooling. No straightening after this anneal is permitted. This procedure is specifically for stress corrosion cracking (SCC) environments, where residual stresses can cause or lead to environmental cracking, particularly in alloys such as 304L and 316L. Frequently the S1 anneal is followed by a magnesium chloride SCC test (ASTM G36) to prove that residual stresses have in fact been eliminated.
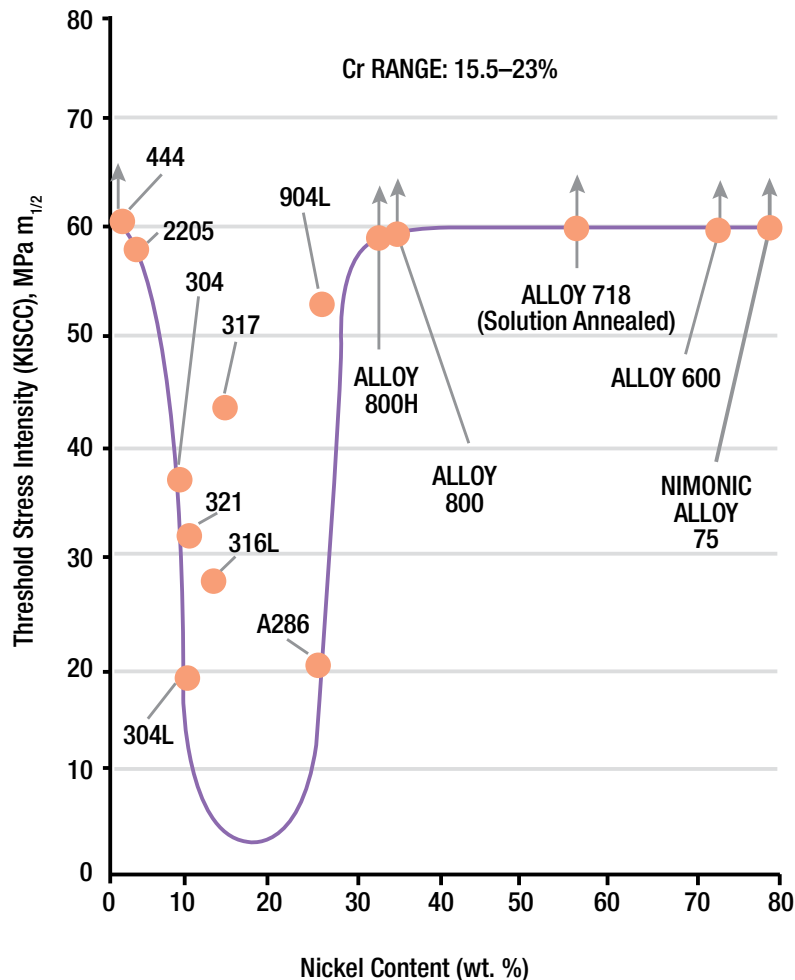
Effect of Nickel content on the stress corrosion cracking threshold stress of various alloys in aerated aqueous 22% NaCl solution at 105°C.

M.O. Speidel, Metallurgical Transactions A. Vol 12A, p779, 1981

Magnetic Permeability

Austenitic stainless steels such as 304L and 316L are nonmagnetic in the annealed, fully austenitic condition. Welds, however, can be mildly magnetic due to retained weld ferrite. Cold working will also generally increase magnetic permeability. Typical magnetic permeability values for alloy 316L tubing are listed below.

Location	Magnetic Permeability @ 200 H (oersteds)	
	Mill Anneal	Extended Anneal
Base Metal	1.01–1.02	< 1.01
HAZ Weld	1.02–1.05	< 1.01
	1.05–1.10	< 1.01

Low magnetic permeability product can be supplied for customers requiring these low values. This is accomplished using extended annealing to reduce the retained weld ferrite.

Contamination by any number of elements can cause discoloration, staining, pitting and poor corrosion resistance. Severe irreparable damage can result from heat-treating with contaminants present. Oils or hydrocarbons often contain chloride ions, which cause general corrosion and pitting. Absorption of carbon can cause sensitization and reduce corrosion resistance in many environments.

Corrosion tests exist for verifying appropriate thermal processing for most alloys. For most stainless alloys such as 304L, 316L, and 317L, ASTM A262 Practices A or E are generally appropriate. A262 addresses inter-granular corrosion resistance in a number of different types of environments depending on the practice (A–E), but all attempt to determine if the material has been sensitized due to inappropriate thermal processing.

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ASTM A262 practice C (Huey test) is a 10-day test for nitric acid service. Alloy 316L will not perform as well as 304L in this service and, in fact, will not pass practice C consistently. For alloy 316L, practices A or E may be more appropriate. Similarly high carbon grades may not be compatible with practice C testing. Stabilized grades are normally tested with practice E.

For duplex stainless steels, ASTM A923 practice A or C may be appropriate. Depending on the service environment, other standard corrosion tests may be appropriate.

ASTM Corrosion Test		Comment	Time	Alloys	Special Processing	Type of Tests
G28	A	Intergranular corrosion susceptibility — Ferric Sulfate — Sulfuric Acid	Alloy dependant	All Alloys		Std Practice
	B	23% H2SO$_4$, 1.2% HCl, 1% FeCl$_3$+ 1% CuCl$_2$,	24 hr	622, 59, 686, 276		Std Practice
G36		Boiling 45% Magnesium Chloride for Stress Corrosion Cracking Resistance (SCC)	24 hr	All Alloys		Std Practice
G48	A	Ferric Chloride (6% FeCl$_3$) pitting test (22 & 50°C)	72 hr Standard	All Alloys	✓✓	Std Practice
	B	Ferric Chloride (6%) **Crevice** corrosion Test (22 & 50°C)	72 hr Standard	All Alloys		Std Practice
	C	Ferric Chloride (6%) Critical Pitting Temperature Test	72 hr Standard	All Alloys		Std Practice
	D	Critical **Crevice** Corrosion Test	72 hr Standard	All Alloys		Std Practice
A249	S7	Weld Decay	1 hr*	304, 316, 317	None laser	Acceptance
A262	A	Detecting Susceptibility to Intergranular Attack — Oxalic Acid Etch Screening				Acceptance & Screening
	B	Detecting Susceptibility to Intergranular Attack — Ferric Sulfate (Streicher Test)		Not for Mo containing		Acceptance
	C	Nitric Acid (65%) (Huey Test)	10 days!!	304L, never 316L	304L	Acceptance
	E	Copper — Copper Sulfate — Sulfuric Acid (A249 S6) (Strauss Test)	24 hr	All Alloys		Acceptance
	F	E with 50% Sulfuric acid for castings	120 hr	All Alloys		Acceptance
A923	A	Sodium Hydroxide Etch Test		Duplex		Acceptance & Screening
	B	Charpy Impact Test, *Requires thick wall!*		Duplex		Acceptance
	C	Ferric Chloride Corrosion test pH=1.3, 25°C for 2205	24 hr	Duplex		Acceptance
Green Death*		11.9% H$_2$SO$_4$ + 1.3% HCl + 1% FeCl$_3$ + 1% CuCl$_2$	72 hr	High nickel pitting alloys		Acceptance

* Not ASTM

For more information, please contact technical representatives at your supplier. If they are unwilling to use standard industry tests to verify appropriate processing or service ability you could be dealing with the wrong supplier. Feel free to contact RathGibson technical personnel at (608) 754-2222 should you have any such questions.

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