HEAT TREATMENT OF STAINLESS STEELS

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1.0 INTRODUCTION

Over a few decades various means of retarding or preventing corrosion of iron and steel products have been extensively used. These include painting or coating with metals or sometimes nonmetals that proved helpful in inhibiting corrosion in specific environments to which the products would be subjected. However, paintings or coatings have limited life. They require periodic replacement to prevent corrosion which will eventually take place.

A desirable approach for minimising or preventing corrosion is by alloying. This not only povides surface protection, but also protection against corrosion throughout the cross-section of the product. A large family of heat and corrosion resisting alloys has been developed to satisfy many requirements for resistance to corrosion, heat or both. These are known as the stainless steels which are iron base alloys containing more than 12% chromium to produce passivity. Various grades of stainless steels thus developed based on alloying would further be subjected to various heat-treating operations to meet all the stringent requirements of design for specific applications especially for their prolonged elevated temperature use.

Heat treatment of such steel serves to produce changes in physical condition, mechanical properties and residual stress level and to restore maximum corrosion resistance when the property has been adversely affected by any previous fabrication or heating. Frequently a combination of satisfactory corrosion resistance and optimum mechanical property is obtained in the same heat treatment. Depending on the room temperature microstructures produced in these steels as a result of various combination of alloying and heat treatments, the steels can be broadly classified into three groups :

- o Austenitic Stainless Steels
- o Ferritic Stainless Steels
- o Martensitic Stainless Steels

2.0 AUSTENITIC STAINLESS STEELS

These steels have f.c.c. structure which is attained through liberal use of austenitizing elements such as Ni, Mn and N. These steels are essentially nonmagnetic in annealed condition and can be hardened only by Cold working. They usually possess excellent cryogenic properties and good high temperature strength. Cr content generally varies from 16 to 26%; Ni upto 35%; and Mn upto 15%. The 200 series steels contain N and 4 - 15% Mn and upto 7% Ni. The 300 series steels contain large amount of Ni and upto 2% Mn. The other elements viz. Mo, Cu, Si, Al, Ti and Nb may be added to confer certain characteristics such as halide pitting resistance or oxidation resistance. S or Se may be added to certain grades to improve machinability.

The austenitic stainless steels may be divided into three groups :

(a) the normal unstabilized composition, such as types 201, 202, 301 to 305, 308 to 310, 316 and 317
(b) the stabilized compositions, principally types 321, 347 and 348 and
(c) the extra-low carbon grades, such as types 304L and 316L. Typical chemical compositions of these steels are given in Table 1.

For the purpose of heat-treating these steels, while loading the products in the furnace, one must take into consideration their high thermal expansion which is about 50% higher than the mild steel. The spacing between the products should be adequate to accommodate this expansion. Stacking, when necessary, should be employed to avoid deformation of the products at elevated temperature.

2.1 Unstabilized Compositions

Steels of 200 series and types 301 - 317 can not be hardened through heat-treatment since their microstructure at room temperature is austenitic. However, these could be hardened by cold working.

Annealing of these steels are carried out to ensure maximum corrosion resistance and to restore maximum softness and ductility. During annealing, carbides, which markedly decrease resistance to intergranular corrosion, are dissolved. Typical ranges of annealing temperatures which vary with composition of the steel are given in Table-2. Since carbide precipitation occurs in the temperature range of 425^{0}C to 900^{0}C, annealing temperature should be maintained safely above this limit. In order to ensure complete dissolution of carbides prior to the start of cooling, the highest practical temperature in the vicinity of 1090^{0}C consistent with limited grain growth must be selected. Cooling from annealing temperature must be rapid and consistent with the limitations of distortion. Whenever considerations of distortion permit, water quenching is used to ensure that the dissolved carbides remain in solution. Steels of types 309 and 310 invariably require water quenching since carbide precipitation in these steels occur more rapidly. Where practical considerations of distortion rule out such a fast cooling rate, cooling in air blast is used. With some thin section size products, the intermediate rate of cooling produces excessive distortion and the products must be cooled in still air. If cooling in still air does not provide a rate sufficient to prevent carbide precipitation, maximum corrosion resistance will not be obtained. A suitable solution to such problem could be the use of stabilized grades of austenitic steels.

2.2 Stabilized Compositions

These steels include types 321, 347 and 348 containing controlled amounts of Ti or of Cb + Ta, which render the steel nearly immune to intergranular precipitation of chromium carbide and its adverse effect on corrosion resistance. These, however, may require annealing to relieve stresses, increase softness and ductility or provide additional stabilization. Typical ranges of annealing temperatures for such steels to obtain maximum softness and ductility are given in Table-2. Unlike the unstabilized grades, these steels do not require water quenching or other acceleration of cooling from the annealing temperature to prevent subsequent intergrannular corrosion. Air cooling is generally adequate. However, section size of product thicker than about $\frac{1}{4}$ inch should be quenched in oil or water to insure maximum retention of austenite.

When maximum corrosion resistance for Ti stabilized (Type 321) and Cb stabilized (Type-347) steels is required, a stabilizing annealing treatment may be employed. This treatment consists of holding at 815^{0}C to 900^{0}C for upto 5 hours depending on section thickness. It may be applied either prior to or in the course of fabrication and may be followed by a short term stress relieving at 705^{0}C without the danger of harmful carbide precipitation. While employing such treatment, certain requirements for proper maintenance of furnace atmosphere must be considered. These are

- o Furnace combustion must be carefully controlled to eliminate carburisation or excessive oxidation.
- o Direct impingement of flame on the work piece must be prevented.
- o Sulphur content of furnace atmosphere must be kept low.
- o Natural gas should be used.

2.3 Extra Low-Carbon Grades

From the view point of precipitation behaviour of Cr-carbides, these grades (Types 304L, 316L and 317L) lie in between the stabilized and unstabilized grades. Very low carbon content (0.03% max) is maintained in these grades to reduce precipitation of intergranular carbides to a safe level. These steels can, therefore, be held in the sensitizing range of 425^{0}C to 815^{0}C for periods upto 2 hours and cooled slowly through this range without the danger of suceptibility to intergrannular corrosion in natural atmospheric environments. Unlike unstabilized grades these steels do not require quenching treatment to retain carbon in solid solution. However, these steels are not suitable for long term service in the sensitizing range because they are not completely immune to the formation of carbides deleterious to corrosion resitance.

Due to the presence of Mo, low carbon grades (316L, 317L) are susceptible to sigma phase formation as a result of long term exposure at 425^{0}C to 815^{0}C. Their corrosion resistance, however, can be improved by employing a stabilizing treatment, consisting of holding at 885^{0}C for 2 hours prior to stress relieving at 675^{0}C. Annealing treatment of these steels are recommended mainly to improve corrosion resistance and to restore softness and ductility. Typical ranges of annealing temperatures are given in Table 2.

3.0 FERRITIC STAINLESS STEELS

These steels are essentially chromium containing alloys with b.c.c. crystal structures. Cr content is usually in the range of 10 to 30%. Some grades may contain Mo, Si, Al, Ti and Nb to confer particular characteristics. S or Se may be added to improve machinability. The ferritic alloys are ferromagnetic. They can have good ductility and formability, but high temperature strengths are relatively poor compared to the austenitic grades. Typical chemical composition of these steels are given in Table-3. These are not appreciably hardenable by quenching but develop maximum softness, ductility and corrosion resistance in the annealed condition. The heat treatment that is mainly applicable to ferritic steels is annealing. The purpose of this heat treatment is primarily to relieve stresses resulting from welding or cold working. Secondly it provides a more nearly homogeneous structure by eliminating patches of transformation product developed during welding or as a result of 475^{0}C embrittlement.

Ferritic steels are annealed at temperatures above the range for 475^{0}C embrittlement and below temperatures at which austenite might form. Typical ranges of annealing temperatures are given in Table-4.

Since ferritic grades can retain austenite or untempered martensite from partial transformation to austenite at high temperatures, Al is added to eliminate such transformation. When ferritic steel (Type 430) is cooled rapidly from 925^{0}C, it may become brittle from austenite transforming to as much as 30% martensite and thus austenite may be retained if it is cooled rapidly from temperatures much above 1090^{0}C. This may be corrected by heat treatment at 650^{0}C to 790^{0}C.

3.1 475 ^{0}C Embrittlement

This causes development of brittleness in ferritic grades, primarily, due to prolonged exposure or slow cooling within the temperature range from 400 to 525^{0}C. Notch impact strength is most adversely affected. The brittleness is believed to be caused by precipitation of a high chromium ferrite and its effects increase rapidly with Cr-content, reaching a maximumm in type 446. Certain heat-treatments, such as furnace cooling for maximum ductility must be controlled to avoid embrittlement. The brittle condition can be eliminated by heat treatment given in Table-4, using temperatures above the upper boundary of embrittlement, followed by rapid cooling to prevent a recurrence.

3.2 Sigma Phase Embrittlement

Sigma phase forms slowly at elevated temperatures in straight Cr-steels containing more than 16% Cr and in Cr-Ni steels containing more than 18% Cr. Sigma phase increases hardness but it decreases ductility, notch toughness and corrosion resistance. The temperature limits for its formation depend on chemical composition and exposure time. There is little evidence that sigma phase develops during heat treatment. However, it is developed in service where long exposure at elevated temperatures are involved. This phase can be redissolved by heating to above $900^{\circ}C$.

4.0 MARTENSITIC STAINLESS STEELS

The heat treatment of martensitic stainless steel is essentially the same as for plain carbon or low-alloy steels, in that maximum strength and hardness depend chiefly on carbon content. The principal metallurgical difference is that the high alloy content of the stainless grades causes the transformation to be sluggish, and hardenability to be so high, that maximum hardness is produced by air cooling in the center of sections upto 12" thick. Typical chemical compositions of these steels are given in Table-5.

The martensitic stainless steels are more sensitive to heat treatment variables than are carbon and low alloy steels. Rejection rates due to fault in heat treating are correspondingly high. Because of initial high cost of these steels and cost of processing them into components, there is no advantage of using them unless superior corrosion resistance is required. The procedures to be followed for quality heat treatment of these steels mainly include prior cleaning, preheating, austenitising and quenching.

4.1 Prior Cleaning

All the components and the fixtures must be thoroughly cleaned before placing them in furnace so as to avoid contamination. This is particularly important when the heat treatment is carried out in a protective atmosphere. Presence of grease and oil may cause carburisation. Stains from finger prints could be a source of chloride contamination and may cause severe scaling in oxidising atmospheres. Furthermore, a protective atmosphere can only be effective when it is permitted to make free contact with metal surfaces.

4.2 Preheating

Martensitic stainless steels are normally hardened by heating above the transformation range to temperatures of 925^{0}C to 1065^{0}C and then cooled in air or oil. Since their thermal conductivity is lower than that of carbon and low alloy steels, development of high thermal gradients and high stresses during rapid heating may cause cracking in some components. To avoid this problem, preheating is usually recommended. Proper care, therefore, should be taken prior to annealing or hardening. The following components should be preheated:

(a) Thin gauge components
(b) Components with both thin and thick sections
(c) Components with sharp corners
(d) Heavily ground components
(e) Components machined with heavy deep cuts
(f) Components that have cold formed and
(g) Previously hardened components.

Preheating is usually carried out at 760^{0}C to 790^{0}C and heating to be continued long enough to ensure that all portions of each component have reached the preheating temperatures. Large heavy components are sometimes preheated at about 535^{0}C prior to preheat at 790^{0}C. Types 403, 410 and 416 require less preheating than the high carbon types 414, 431, 420 and 440 grades.

4.3 Austenitizing

The range of austenitising temperatures, quenching mediums as well as the range of tempering temperatures for various grades of martensitic stainless steels are summarized in Table-6. When maximum corrosion resistance and strength are desirable, the steel should be austenitized at the higher end of the temperature range. Steels of types 403, 410 and 416 show an increasing trend of hardness with austenitising temperature upto about 980^{0}C and thereafter the hardness decreases because of austenite retention and occasionally the formation of delta ferrite.

Soaking times employed in hardening represent a compromise between (a) achieving maximum strength and corrosion resistance due to

Soaking times employed in hardening represent a compromise between (a) achieving maximum strength and corrosion resistance due to dissolution of chromium carbides and (b) avoiding decarburisation, excessive grain growth, retained austenite, brittleness and quench cracking. For sections upto $\frac{1}{2}$ inch thick, soaking time of 30 to 60 minutes is sometimes recommended. Additional soaking of 30 minutes for each additional inch of thickness or fraction thereof has proven adequate. However, soaking period should be doubled if the components to be hardened have been fully annealed or isothermally annealed.

4.4 Quenching

All martensitic stainless steels can be quenched in either oil or air. Oil quenching guarantees maximum corrosion resistance and ductility in all alloys. Some decrease in corrosion resistance and ductility, resulting from air cooling may occur in Types 414, 420, 431 and 440 grades. These steels may precipitate carbides in grain boundary areas if heavy sections are cooled slowly through the temperature range of 870^{0}C to 538^{0}C. This may impair their corrosion resistance. Although oil quenching is preferred, air cooling may be required for heavy sections to prevent distortion or quench cracking.

Martempering is particularly easy with these steels because of their high hardenability.

The higher carbon martensitic grades (Type 440) and higher - Ni (Type 431) are likely to retain about 30% untransformed austenite in the as quenched structure. A portion of austenite retained in quenching may be transformed by sub-zero cooling to about -73^{0}C immediately after quenching. To obtain maximum transformation of retained austenite, two or more complete tempering cycles are necessary after subzero cooling. components should be air cooled to room temperature between the tempering cycles.

Table — 1. Typical Chemical Composition of Austenitic Stainless Steels

Type	C	Mn	Si	Cr	Ni	P	S	Others
				Unstabilised Compositions				
201	0.15	5.5-7.5	1.00	16.0-18.0	3.5-5.5	0.06	0.03	0.25N
301	0.15	2.00	1.00	16.0-18.0	6.0-8.0	0.045	0.03	—
304	0.08	2.00	1.00	18.0-20.0	8.0-10.5	0.045	0.03	—
309	0.20	2.00	1.00	22.0-24.0	12.0-15.0	0.045	0.03	—
310	0.25	2.00	1.50	24.0-26.0	19.0-22.0	0.045	0.03	—
314	0.25	2.00	1.5-3.0	23.0-26.0	19.0-22.0	0.045	0.03	—
316	0.08	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2-3.0Mo
317	0.08	2.00	1.00	18.0-20.0	11.0-15.0	0.045	0.03	3-4.0Mo
				Stabilised Compositions				
321	0.08	2.00	1.00	17.0-19.0	9.0-12.0	0.045	0.03	5X%C min. Ti
347	0.08	2.00	1.00	17.0-19.0	9.0-13.0	0.045	0.03	10X%C min. Nb
348	0.08	2.00	1.00	17.0-19.0	9.0-13.0	0.045	0.03	0.2Co; 10X%C min. Nb; 0.10Ta
				Extra Low Carbon Grades				
304L	0.03	2.00	1.00	18.0-20.0	8.0-12.0	0.045	0.03	—
316L	0.03	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo
317L	0.03	2.00	1.00	18.0-20.0	11.0-15.0	0.045	0.03	3.0-4.0 Mo
316LN	0.03	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo; 0.10-0.16 N

Table—2. Recommended Annealing Temperatures for Austenitic Stainless Steel

Type	Temperature, ^0C
Unstabilised Compositions	
201	1010 - 1120
301	1010 - 1120
304	1010 - 1120
309	1040 - 1120
310	1040 - 1065
314	1040 - 1120
316	1040 - 1120
317	1065 - 1120
Stabilised Compositions	
321	955 - 1065
347	985 - 1065
348	985 - 1065
Extra Low Carbon Grades	
304L	1010 - 1120
316L	1040 - 1110
317L	1040 - 1110

Table — 3. Typical Chemical Composition of Ferritic Stainless Steels

Type	C	Mn	Si	Cr	Ni	P	S	Others
405	0.08	1.00	1.00	11.5-14.5	-	0.04	0.03	0.1-0.3Al
409	0.08	1.00	1.00	10.5-11.7	0.50	0.045	0.045	6X%C min.- 0.75max, Ti.
429	0.12	1.00	1.00	14.0-16.0	-	0.04	0.03	—
430	0.12	1.00	1.00	16.0-18.0	-	0.04	0.03	—
430F	0.12	1.25	1.00	16.0-18.0	-	0.06	0.15 min.	0.6 Mo
442	0.20	1.00	1.00	18.0-23.0	-	0.04	0.03	—
446	0.20	1.50	1.00	23.0-27.0	-	0.04	0.03	0.25 N

Table—4. Recommended Annealing Temperatures for Ferritic Stainless Steel

Type	Temperature, ^{0}C
405	650 - 815; AC or WQ
430	705 - 785; AC or WQ
	or 815 - 900; FC to 595; AC
430F	705 - 785; AC or WQ
442	760 - 830; AC or WQ
446	760 - 830; AC or WQ

NB: AC: air cool; WQ: water quench; FC: furnace cool.

Time at temperature depends on section thickness, but is usually 1 to 2 hour except for sheet, which may be soaked 3 to 5 minutes per 0.1 in of thickness.

Table — 5. Typical Chemical Composition of Martensitic Stainless Steels

Type	C	Mn	Si	Cr	Ni	P	S	Others
403	0.15	1.00	0.50	11.5-13.0	-	0.04	0.03	-
410	0.15	1.00	1.00	11.5-13.5	-	0.04	0.03	-
414	0.15	1.00	1.00	11.5-13.5	1.25-2.50	0.04	0.03	-
416	0.15	1.25	1.00	12.0-14.0	-	0.06	0.15 min.	0.6 Mo
416Se	0.15	1.25	1.00	12.0-14.0	-	0.06	0.06.	0.15 min. Se
420	0.15 min.	1.00	1.00	12.0-14.0	-	0.04	0.03	-
431	0.20	1.00	1.00	15.0-17.0	1.25-2.50	0.04	0.03	-
440A	0.06-0.75	1.00	1.00	16.0-18.0	-	0.04	0.03	0.75 Mo
440B	0.75-0.95	1.00	1.00	16.0-18.0	-	0.04	0.03	0.75 Mo
440C	0.95-1.20	1.00	1.00	16.0-18.0	-	0.04	0.03	0.75 Mo

Table — 6. Recommended Hardening and Tempering Temperatures for Martensitic Stainless Steels

Type	Austenitising temperature, ^0C	Quenching Medium	Tempering Temperature, ^0C
403	925 - 1010	Air or oil	565 - 605
410	925 - 1010	Air or oil	565 - 605
414	925 - 1050	Air or oil	595 - 650
416	925 - 1010	Oil	565 - 605
416Se	925 - 1010	Oil	565 - 605
420	985 - 1065	Air or oil	205 - 370
431	985 - 1065	Air or oil	565 - 605
440A	1010 - 1065	Air or oil	150 - 370
440B	1010 - 1065	Air or oil	150 - 370
440C	1010 - 1065	Air or oil	165 max.