CHAPTER II

LITERATURE SURVEY

AUSTENITIC STAINLESS STEELS

2.1. PASSIVITY

The remarkable corrosion resistance exhibited by metals like; aluminum titanium, chromium, iron, nickel and their alloys, which make them industrially significant materials. The corrosion resistance in most of these metals and alloys is usually related to the formation of thin passive films on the metal surface, which exhibit semi-conducting or insulating properties. The passive films are interesting because they ensure protection from the very process responsible for their formation (1).

Almost all metals/alloys undergo corrosion in one or the other environment. This depends upon oxidation power/ionizing capacity of the metals and electrochemical power or aggressiveness of the media. In general, corrosion is more significant in acidic media compared to others. On the other hand, high corrosion resistance to wide range of environments is observed in those metals/alloys, which exhibit active-passive transition. Also a minor change in composition of metal/alloy or environment, sometimes dramatically alters their corrosion behavior.

Many metals and their alloys achieve active-passive state in different media and conditions. But the degree of passivity attained will be different in each case. Most commonly the active metals and their alloys quickly attain complete passive state in favorable conditions. Once the passive film has been nucleated on a metal surface, the further growth, nature and behavior of film depends on the chemical, electrical and mechanical properties of the film substance. The most complete passivity is achieved (2), in general, when the film substance has:

- Low ionic conductivity,
- Appreciable electron conductivity
- Stability over a wide range of potential.
- High compressive strength
- Very low chemical slubility/dissolution rate.
- Tenacious and well adherent to metal surface.

If metal alone doesn't meet the above requirements fully, suitable alloying addition may impart few or all of these properties.

Both Austenitic Stainless Steel and Titanium, selected for investigation in the present work, are exhibiting active-passive transition under certain conditions of environment. Passivity or state of inactivity is attained by these materials is primarily due to contention of thin film on their surfaces. Film may be generated by adsorbed oxygen or other gas or ions or due to change in electronic configuration atoms on the surface, which makes a stable oxide film. However, metal beneath the film still remains active. Therefore, main factors accounting for passivity behavior of these metal and alloys are the nature, quality and mechanism involved in formation of the film.

2.1.1 MECHANISM OF PASSIVATION

Passivity is a complex concept and clear-cut definition is difficult to give. In the simple terms, passivity implies that under some special conditions a metal or alloy will behave as an inert material, which otherwise is very reactive ones. The nature of passivity is in dispute, several phenomena have been put forth and explanations are given. By and large most scientists embrace the "oxide film" theory. According to this theory, reaction with its environment covers a metal or alloy with corrosion product and converts it in the passive state. This covering act as a barrier between metal and its ambient surrounding thereby reduces its dissolution rate.

Passivity may be substantial or partial, in the sense that either the metal surface undergoes covering by corrosion product at much slow rate than dissolution rate of metal or some areas become passive while other remains active. Such events depend upon the characteristics of the film formed. In former case film may be porous while in later it may be fragile or poorly adherent. Here the substrate or underneath metal also plays its role, any defect on the surfaces like; inclusion, vacancies, slip planes and precipitation may not be passivated like rest of the surface areas and lead to galvanic cell, resulting in localize corrosion. As film is forming by corrosion product, the amount of charge needed to produce passivation governs the thickness and nature of the films generate on the freshly prepared metal surfaces (3). Evidently, the nucleation and growth of the film substance are vitally important in deciding how thick, compact and stable film will be finally formed and what degree of passivity it will provide.

. An examination of nature of the passive films is of prime importance to the understanding of corrosion behavior and for devising measures for corrosion prevention and control. The chemical composition and structural properties of passive films can be obtained from surface analytical techniques, which are ex-situ measurements and are subjected to considerable ambiguity. However, Photo Electrochemical (PEC) and Electrochemical Impedance Spectroscopy (EIS) techniques have proven to be attractive techniques for probing the passive films in-situ [4] for identifying the film's chemical composition and obtaining useful information regarding their electronic and other properties, which may significantly influence the films behavior.

The passive films on Fe-Cr alloys have predominantly an outer a-Fe_20_3-like layer whose thickness reduced as the Cr content in the alloy increased. The addition of first row of transition metals (having partially filled 3d shell) like; V, Cr, Mn, Fe, Co, Ni and Cu to Ti was found to affect only the magnitude of the photocurrent with no marked changes in the band gap, except Ti & V alloys (5). The passive films of these alloys were similar to impurity doped TiO2, e.g., Cr: TiO2, Mn: TiO2 etc. For Fe-Mo alloys, the passive films behaved similarly as the film on pure Fe in absence of Cr and appeared to be independent of Mo addition (6).

Passive film of ASS is very thin (10-50 °A) and is oxide/hydrous oxides type. As compared with composition of matrix, films are enriched with Cr, Mo and Si. Normally films are virtually free of pores, but their stability may be weakened considerably locally. Structure of film corresponds to that of the underlying metal and will therefore have different properties in areas where steel surface is disturbed or impaired as stated above.

Passivation requires entire surface to be reached by sufficient oxidizing agent. Should any substances, such as foreign objects, shield any part then concentration gradient may arise requiring high oxidizing agents. Therefore surface should be clean and free from mill scale or deposits.

A convenient way to understand the passivity is by considering the potential - current density diagram, generally known as a "polarization curve". Metal/alloy, when exposed to the atmosphere, develops a passive oxide film on the surface, which prevents ionic transfer through it. Anodic polarization curve can explain the phenomena of passivity, in potentiostatic measurement current density attains a reduced value at a critical voltage and retain it over a range of potential, while in galvanostate measurement potential remains constant at a critical value of current and retained it over a span of current. Such constant voltage or current over a span of the other is called attainment of passivity in the given metal-environment system.

2.1.2. Theories of Passivity

The electrochemical behavior of metal exhibiting passivity is fairly well understood, though the cause of passivity is still debatable. Two main theories are briefed below:

I *Oxide-Film Theory [7,8]:*

According to this theory the corrosion product, usually a metal oxide acts as a diffusion barrier and slows down the corrosion rate by effectively separating the metal from the environment. This film is often very thin and invisible. Thus, when the passive state is established the physiochemical properties of the metal relative to the environment depend to a large extent on the properties of the protective film.

II *Adsorption Theory [9,10]*

According to this theory, passivity is cause due to an adsorbed film of oxide or other passivating agents, which decreases the exchange current density and increases the anode over voltage for the anodic oxidation reaction (M --> M^+ +e^-). Such a layer displaces adsorbed HO molecules and slows down the rate of metal hydration and thereby corrosion rate. This theory, without rejecting the possibility of anodic film formation responsible for passivity describes anodic inhibition as an electrochemical mechanism.

Tomashov and Chernova (11) have pointed out that the oxide film and adsorption theories do not contradict, but rather supplement each other. As the adsorbed film in the process of thickening gradually passed into an oxide film, the retardation of the anodic processes promoted by the change in double layer structure will also be supplemented by the greater difficulty encountered in passage of ions directly through the protective film. Undoubtedly, depending on the natures of the metal and environment there could be variations in the thickness of the protective film.

2.1.3 Factors Affecting Passivity of ASS:[12,13]

I: Metallurgical factors:

(A) *Chemical composition*

Passivation characteristics of metal are influenced by the presence of alloying elements. Fig 2.1 shows schematically the anodic polarization curves for Fe and Cr in an acid [13]. Fe is passivatted only at high positive potentials and also requires a high critical current density. However, the trans-passive potential lies at very high values, Cr is much easier to passivate, since Ep is considerably lower, approximately 0.5 V, and Ic is several orders of magnitude lower. In short raising the Cr content confers the following benefits:

1) Lower passivity potentials (E_{pp}),
2) Reduced passive current density (I_{pp}),
3) Higher breakdown and pitting potentials (E_{bk}), and
4) Lower critical current density (I_{crt}).

Alloying of Fe with **Chromium** moves the primary passive potential (E_{pp}) in the active direction, expanding the passive potential range and reduces the passive current density. Effect of Cr-additions on the anodic polarization behavior is illustrated noticeably by the data shown in fig.2.2 for a series of Fe-Cr alloys in a sulfuric acid solution (14). The effect of common alloying elements on the anodic polarization curve of the ASS in an acid-chloride solution is schematically summarized in fig 2.3.

Molybdenum moves the pitting potential in the noble direction, thereby extending the passive potential range and lowering critical current density. Type SS 304 is difficult to passivate while type SS 316 can easily be passivated (fig.2.4). **Nitrogen** additions to Mo free Austenitic stainless steel are beneficial to the development of passivity in sulfuric acid solutions (fig.2.5). Nitrogen moves the pitting potential in the noble direction, thereby extending the passive potential range. **Mn** is generally considered detrimental to the pitting resistance of ASS due to the formation of MnS. The combined beneficial effects of Mo and Nitrogen tend to override this detriment, and the pitting potentials exhibit high noble values, (i.e. type SS 216).

Nickel in ASS steels promotes a decrease in the passive current (I_{cnt}) and the active range -is contracted and shifts the passive potential (E_{pp}) in the favorable direction, fig. 2.6. Other alloying elements that move the pitting potential in the noble direction thereby extending the passive potential range are V, Si and W.

More recently, **tungsten** has also been shown to extend the passive potential range and reduce the passive current density. **Copper** is added to Ass for improving the corrosion resistance in sulfuric acid environments.

The passive film on ASS could be destroyed if certain active ions such as halide ions are present. This is caused because potential reaches a value, at which the passive film destroyed, known as "breakdown potential"(E_{br}). This causes pitting formation.

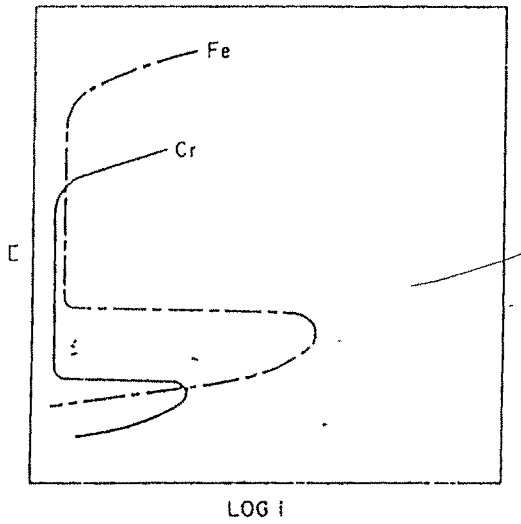


FIG. 2.1 Effect of Cr and Fe content on their anodic polarization curves.

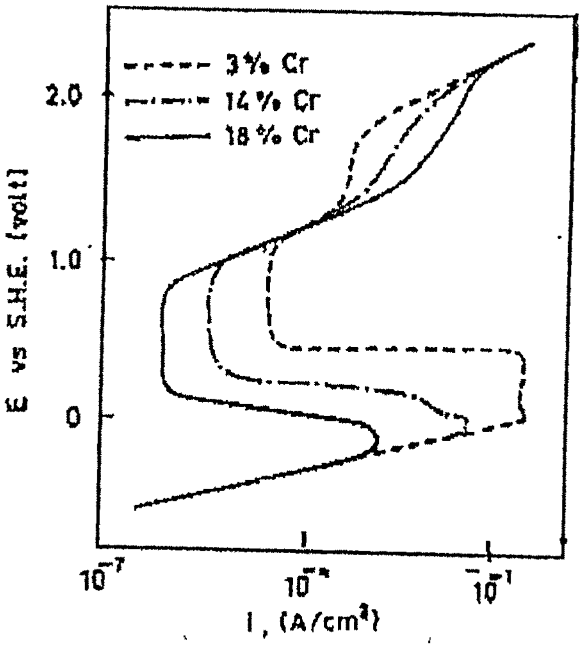


FIG. 2.2 Effect of chromium content on anodic polarization curve of Fe-Cr alloys in 10% H_2SO_4 at 21°C

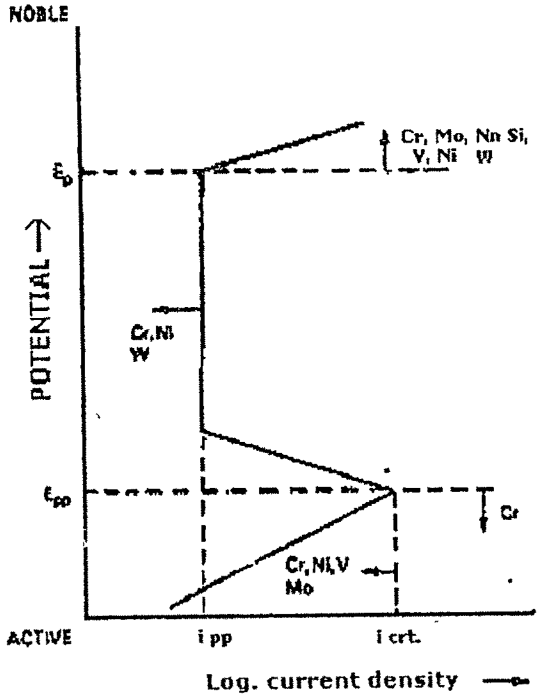


FIG.2.3: Schematic summery of the effect alloying elements in SS on the anodic polarization curve.

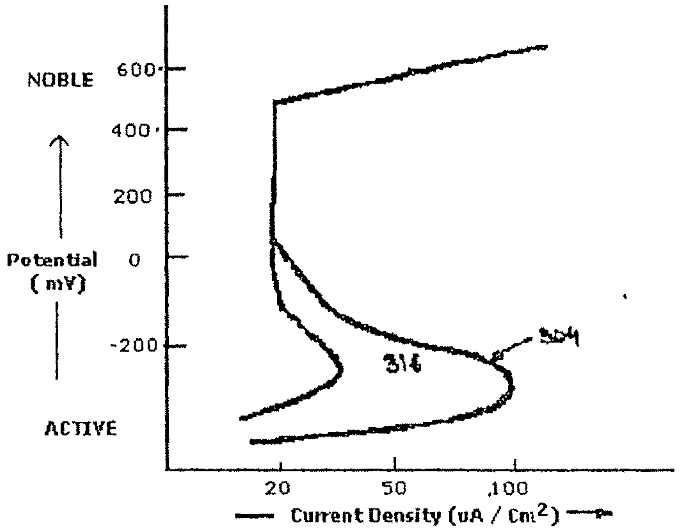


FIG-2.4 : Anodic Polaruzation Curves for SS type-304 & 316 in 5% sulfuric acid at 25 °C

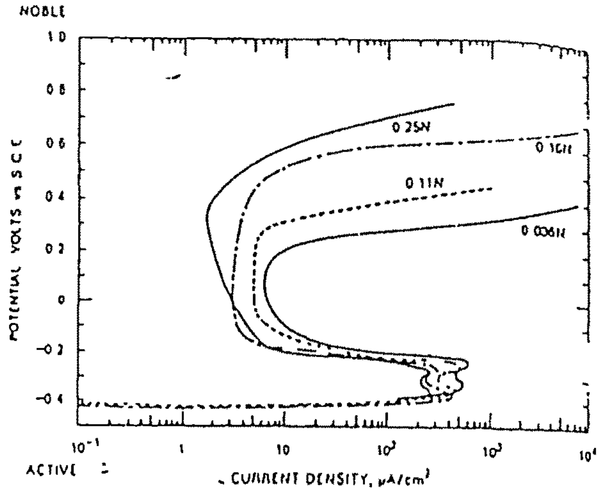


FIG. 2.5 Anodic polarization curves for 18% Cr-8%Ni SSs Containing various of nitrogen, tested in a hydrogen purged 1 N H_2SO_4 + 0.5 M NaCl solution at ambient temperature (from Eckenrod and Kovach).

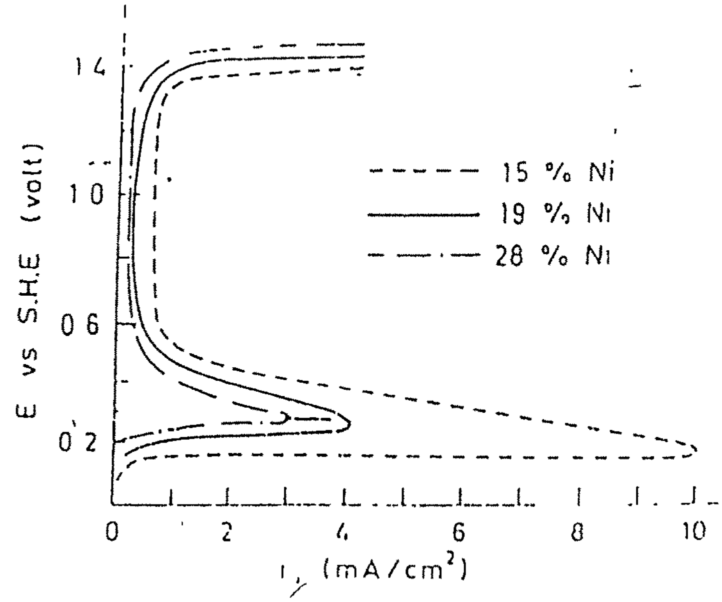


FIG. 2.6 Effect of nickel content on anodic polarization curves of 9% Cr-3% Mo-3% Cu steel in 12N H_2SO_4, at 60°C [Bozin and Kurtepov] [37]

If the rate of passive film dissolution is high, the anodic current in the passive state will also be quite high. Typical example is ASS in a mixture of Nitric acid and hydro fluoric acids a condition invariably represents in electro-polishing.

(B) *Heat treatment*: Annealing increases the passive range and lowered E_{pp} value.. Cold working reduces the passive potential range

(C) *Environmental Factors:*

(a) Stirring rate of Electrolyte: Stirring of electrolyte increases corrosion rate

(b) Temperature and pH of Electrolyte: An increase in temperature and pH of electrolyte generally:

♦ Reduces the passive range.

♦ Increases the critical current density for passivation i_{cnt}

♦ Increases corrosion rate (i.e. i_{corr}) in the passive range.

. A similar effect is noticed upon increasing chloride additions in the case of ASS. In some cases it might result in complete loss of passivity. Under strongly oxidizing condition passivity increases. If oxidizing conditions are maintained only by dissolved oxygen in environment, then temperature rise will reduce the oxygen content and thereby reduces ease of passivity. In case of SS 304 in 67% H2S04 critical current density for passivation decreases with increases in temperature.

(c) Addition of oxidizers: Presence of oxidizers enhances passivity.

(d) Presence of halogen ions: Fig. 2.7 shows ASS in chloride free aqueous sulfuric acid and chloride containing sulfuric acid. The introduction of chloride ion lowers the noble extreme of the passive range to that of the pitting potential. Figure shows the current " breaks" at somewhat lower (more active) potentials. This "break through" is accompanied by the formation of corrosion pits. On the rest specimen surface and is usually known as the pitting potential "E_{pit}".

Presence of chloride and to a lesser extent other halogen ions (B, I etc) destroy passivity in ASS. Among these F-ions are most aggressive, till it does not form complexes.

(e) Cathode over voltage : A decrease in cathode over voltage causes decrease in corrosion rate due to attainment of passivity (which is shown in fig. 2.8) as the over voltage decrease from 1 to 4 a decrease in corrosion rate due to passivity could be observed. This is achieved simply by addition of noble alloying element/s.

(f) Aeration: Dissolved oxygen can be increased by aeration, which in turn increases passivity.

(g) Abrasion: If passive film is continually worn off and reforms rapidly then passivation is maintained.

Oxidizing potential of acid must be high for easy passivation. Passivity creation requires high oxidizing potential where as passivity retention requires low over oxygen potential.

2.2 THE STAINLESS STEEL

The "stainless" or corrosion resistance adornment to steel is derived principally from the element chromium (12,15). The passivity of stainless steels is confined to the surface of the alloy, and it is beli0eved due to presence of protective films whose existence depends on a continuous supply of Cr and O_2 atoms. Theories differ in respect to the nature of this protective layer; one postulate that the oxygen is present as a physically adsorbed film, a second as a chemi-adsorbed layer and a third, as the compound chromium oxide. In either case chromium and oxygen must be available, if the layer has to be effective.

The concentration of chromium in the film is observed to be higher than in metal and both chromium content and film thickness increase with increasing polish (16). These observations account very well for the practical fact that the higher the polish, better be the corrosion resistance of stainless steels. Passivity appears sharply when dissolved chromium exceeds about 11.5% and improves gradually with increasing chromium content. Chromium should be available as dissolved in iron and not in the locked form as oxide or compound, if it is to be effective. This "passive film" provides the corrosion resistance and is self-healing type in a wide variety of environment.

Today more than 180 different alloys can be recognized as belonging to the stainless steel group, and each year a new one and/or modifications of existing ones appear. In some stainless steels the chromium content now approaches 30%. The other elements are added to provide specific properties following are the few examples:

*	Nickel, Nitrogen and molybdenum	for corrosion resistance
*	Carbon, Molybdenum, Nitrogen, Titanium, Aluminum and Copper	for strength and high temperature properties
*	Sulfur and Selenium	for machinability
*	Nickel	for formability and Toughness.

2.2.1 TYPES OF STAINLESS STEEL

It is customary to divide the more common stainless steels into three groups according to metallurgical structure. A simple, although somewhat approximate, way to relate metallurgical structure with the composition of stainless steels is by means of Schaeffler diagram, shown in figure-2.9.

This diagram indicates the structure obtained after rapid cooling to room temperature from elevated temperature and is not an equilibrium diagram. It was originally established to estimate the delta ferrite (It is ferrite formed on rapid solidification, as opposed to alpha ferrite, which is transformation product of austenite or martensite). In establishing this diagram, the alloying elements commonly found in stainless steels are regarded either as austenite stabilizers or as delta ferrite stabilizer.

The relative "potency" of each element is conveniently expressed in terms of equivalence of either nickel (austenite stabilizer) or chromium (ferrite stabilizer)

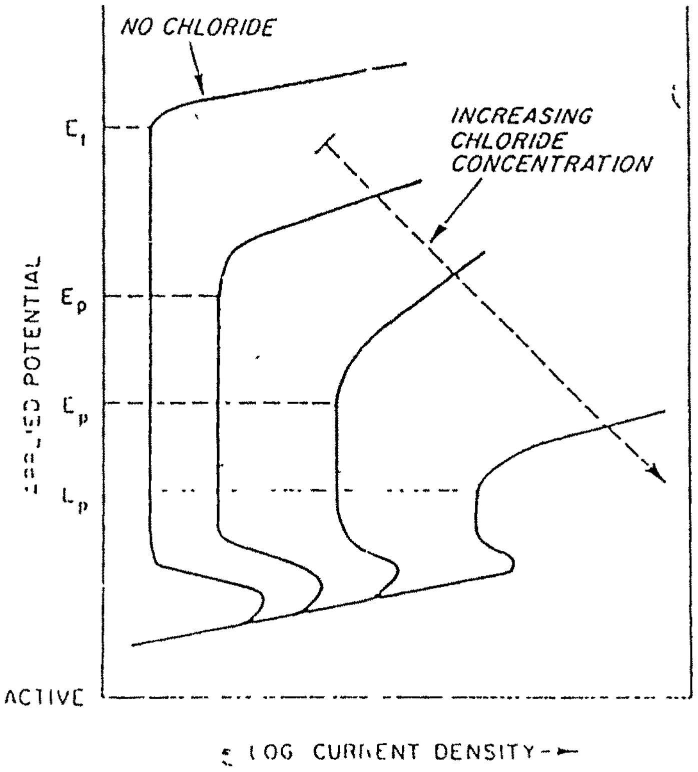


FIG. 2.7 Typical polarization curves for a stainless steel in sulfuric acid solution containing increasing amounts of chloride.

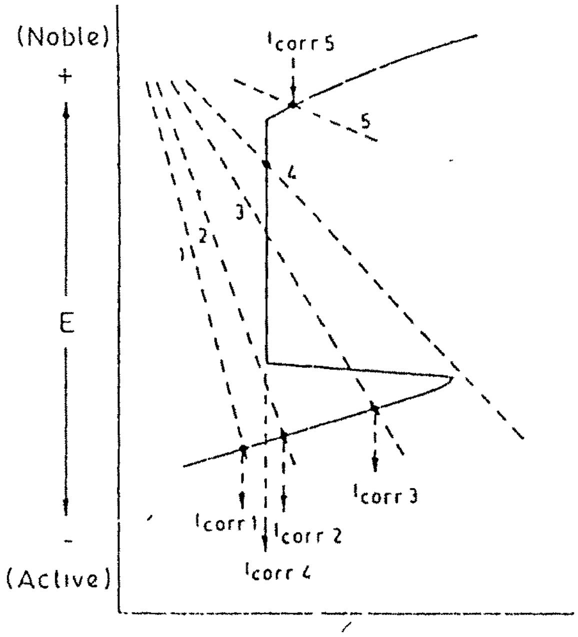


FIG. 2.8 Effect of cathodic over-voltage on the corrosion rate of a metal exhibiting passivity.

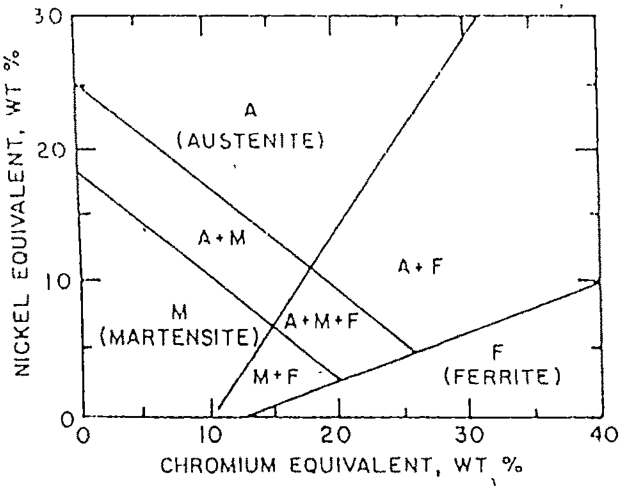


FIG 2.9 SCHAEFFLER DIAGRAM

on weight percentage basis. The nickel and chromium equivalents form the two axes of Schaeffler diagram.

2.2.2 FAMILIES OF STAINLESS STEELS:

There are five major families of stainless steels based on crystallographic structure (17).

2.2.2.1 *Ferritic Stainless steel*:

The simplest steels contain only iron and chromium, chromium is ferrite stabilizer, and therefore, the stability of the ferritic structure increases with chromium content AISI 400 series, include steels with minimum of 11.5% chromium and not more than 2.5% of other alloying elements. These are known as high *chromium irons* or *straight chromium steels,* and are further divided into the hardenable (martensitic) and non-hardenable grades.

- Ferrite has a BCC crystal structure.
- It is characterized as magnetic material.
- It has relatively high in yield strength, low ductility and work hardenability
- Ferrite shows low solubility for interstitial element such as carbon and nitrogen
- The ferritic grades exhibit a transformation from ductile to brittle behavior over a rather narrow temperature range

The ferritic family was then limited to AISI type 446 for oxidation resistant application and to AISI type 430 and 434 for corrosion resistant applications.

2.2.2.2 *Austenitic Stainless steels*:

The detrimental effects of carbon and nitrogen in ferrite can be overcome by changing the crystal structure to Austenite, a FCC crystal structure. This change is accomplished by adding Austenite stabilizer most commonly issued is nickel but also manganese and nitrogen in combination are also used

- Austenite is characterized as nonmagnetic.

- It is relatively low in yield strength with high ductility, rapid workhardening rates, and excellent toughness.
- It is easy to fabricate.

  AISI 300 series, including steels with minimum 17% Cr and 8% Ni and in which alloying elements are balanced to provide additional desired properties, retaining austenitic (FCC) structure. These are also known as *chromium-nickel austenitic stainless steels.*

  AISI 200 series, containing steels which are modification of AISI 300 series; the nickel content has been reduced the austenitic structure is stabilized by increasing manganese and nitrogen contents. These steels are also known as *chromium-nickel-manganese/nitrogen austenitic stainless steels*

2.2.2.3 *Martensitic Stainless Steels:*

With lower chromium levels and relatively high carbon levels. It is possible to obtain Austenite at elevated temperatures then, with rapid cooling, to transform this Austenite to Martensite, which has a body, centered tetragonal structure.

- In plain carbon and low alloy steels, this strong, brittle martensite can be tempered to favorable combination of high strength and toughness. The corrosion resistance is limited
- Nitrogen, nickel and molybdenum additions at somewhat lower carbon levels have produced martensitic stainless steels with improved toughness and corrosion resistance.

2.2.2.4 *Duplex stainless steel:*

It is a chromium-molybdenum ferritic stainless steels to which austenitic stabilizer have been added in which a balance amount of ferritic and austenite are present at room temperature.

Chemical Analyses of Stainless Steels, per cent

AISI No.	*Carbon*	*Manganese*	*Silicon*	*Chromium*	*Nickel*	*Other Elements*
Chromium-Nickel-Magnesium-Austenitic—Non-Hardenable						
201	0.15 max	5 5/7 5	1 0	16.0/18 0	3.5/5.5	N_2 0.25 max
202	0.15 max.	7.5/10	1.0	17.0/19.0	4 0/6 0	N_2 0.25 max
Chromium-Nickel-Austenitic—Non-Hardenable						
301	0.15 max.	2 0	1 0	16.0/18.0	6.0/8.0	—
302	0.15 max.	2.0	1.0	17.0/19.0	8 0/10.0	—
302B	0.15 max.	2 0	2.0/3.0	17.0/19.0	8.0/10.0	—
303	0 15 max	2.0	1.0	17.0/19.0	8.0/10.0	S 0.15 min
303Se	0.15 max.	2 0	1 0	17.0/19.0	8 0/10 0	Se 0.15 min
304	0 08 max.	2.0	1.0	18.0/20.0	8 0/12 0	—
304L	0.03 max	2.0	1.0	18.0/20.0	8.0/12 0	—
305	0 12 max.	2 0	1 0	17.0/19.0	10 0/13 0	
308	0.08 max.	2.0	1.0	19.0/21.0	10.0/12.0	—
309	0.20 max.	2.0	1.0	22.0/24.0	12 0/15 0	—
309S	0 08 max	2 0	1 0	22.0/24 0	12.0/15 0	—
310	0.25 max.	2 0	1 50	24.0/26 0	19 0/22 0	—
310S	0 08 max	2 0	1.50	24.0/26.0	19 0/22 0	—
314	0.25 max.	2 0	1.5/3.0	23.0/26.0	19.0/22.0	—
316	0.08 max.	2.0	1 0	16.0/18.0	10 0/14.0	Mo 2 0/3.0
316L	0.03 max.	2.0	1.0	16 0/18 0	10.0/14.0	Mo 2 0/3 0
317	0 08 max	2 0	1.0	18 0/20.0	11 0/15 0	Mo 3.0/4.0
321	0.08 max	2 0	1.0	17 0/19 0	9 0/12.0	Ti 5×C min
347	0.08 max	2.0	1 0	17 0/19 0	9 0/13 0	Cb+Ta 10xC min.
348	0.08 max.	2.0	1.0	17.0/19.0	9.0/13.0	Ta 0 10 max
Chromium-Martensitic—Hardenable						
403	0.15 max	1.0	0.5	11.5/13 0	—	—
410	0.15 max	1 0	1.0	11.5/13 5	—	—
414	0.15 max	1.0	1.0	11.5/13 5	1.25/2 5	—
416	0.15 max	1.25	1.0	12.0/14.0	—	S 0.15 min
416Se	0.15 max	1 25	1.0	12.0/14.0	—	Se 0 15 min
420	Over 0 15	1 0	1.0	12.0/14.0	—	—
431	0.20 max	1 0	1 0	15 0/17 0	1.25/2 5	—
440A	0.60/0 75	1 0	1.0	16.0/18 0	—	Mo 0 75 max
440B	0.75/0 95	1.0	1.0	16.0/18 0	—	Mo 0.75 max
440C	0.95/1 2	1.0	1 0	16 0/18.0	—	Mo 0 75 max
Chromium-Ferritic—Non-Herdenable						
405	0.08 max	1 0	1 0	11 5/14.5	—	Al 1 1/0 3
430	0 12 max	1 0	1.0	14.0/18 0	—	—
430F	0 12 max	1 25	1 0	14 0/18 0	—	S 0.15 min
430FSe	0 12 max	1 25	1 0	14.0/18 0	—	Se 0.15 min
446	0 20 max	1 50	1.0	23.0/27.0	—	N_2 0 25 max
Martensitic						
501	Over 0.10	1 0	1.0	4.0/6.0	—	Mo 0 40/0 65
502	0 10 max	1 0	1.0	4 0/6.0	—	Mo 0 40/0 65

TABLE 2 COMPOSITIONAL & PROPERY LINKAGES IN THE STAINLESS STEEL FAMILY OF ALLOYS.

- It can have the high chromium and molybdenum responsible for the excellent corrosion resistance of ferritic stainless steels as well as the favorable mechanical properties of austenitic stainless steel.
- The duplex grade with about equal amount of ferrite and austenite have excellent toughness and their strength exceeds to that of either phase present singly.
- It has high corrosion resistance, good resistance to chloride SCC.
- It has good production economy in heavier product forms.

First generation duplex grade, such as AISI type 329, achieved this phase balance primarily by nickel additions. The addition of nitrogen to the second generation of duplex grades restores the phase balance more rapidly and minimizes chromium and molybdenum segregation without annealing. The newer duplex grades combine high strength and good toughness.

2.2.2.5 *Precipitation-hardening stainless steels:*

These are chromium-nickel grades that can be hardened by an aging treatment at moderately elevated temperature. These grades have austenitic, Semi austenitic or martenisitic crystal structure. Semi-austenitic structure is transformed from a readily formable austenite to martensite by a high temperature austenite conditioning treatment. Some grades use cold works to facilitate transformation

- The strengthening effect is achieved by adding copper and aluminium, which forms intermetallic, precipitates during aging.
- In the solution annealed condition these grades have properties similar to austenitic grades and are therefore readily formed.
- Hardening is achieved after fabrication within relatively short time at 480 degree centigrade to 620 degree centigrade.
- The precipitation hardened grades have corrosion resistance generally comparable to that of the chromium nickel grade.

2.2.3 TYPES OF AUSTENITIC STAINLESS STEELS:

Nickel Stainless Steel (300Series): The 300 series represents by for the largest category of stainless steels. The compositions of the steels in the 300 series are shown in table 2.1. The 300 series represent compositional modifications of the classic 18/8 (18% Cr- 8% Ni) stainless steel. Among the more important compositional modifications that improves corrosion resistance are:

→ Addition of molybdenum or molybdenum plus nitrogen to improve pitting and crevice corrosion resistance.

→ Lowering the carbon content or stabilizing with titanium or niobium plus titanium to reduce intergranulur corrosion in welded materials.

→ Addition of nickel and chromium to improve high temperature oxidation resistance and strength.

The **type 304** is the general-purpose grade, widely used in application requiring a good combination of corrosion resistance and formability.

Type 301 exhibits increased work hardening on deformation and is used for higher strength application.

Type 302 is essentially the higher carbon version of type 304, which yields higher strength on cold working. The 302B have a higher silicon content and greater oxidation resistance in high-temperature application.

Type 303 and **303 Se** contains sulfur and selenium, respectively, and are the free - machining grades used in applications where ease of machining and good surface finish is important. Type 303 Se is also used in applications requiring hot upsetting because of its good hot workability under this condition.

Type 304L is a lower carbon modification of type 304 used in application requiring welding. The lower carbon content minimizes carbide precipitation in the HAZ near welds, which can lead to 1GC in certain environment.

A farther modification of 304 is type **304N**, to which nitrogen is added to enhance the strength.

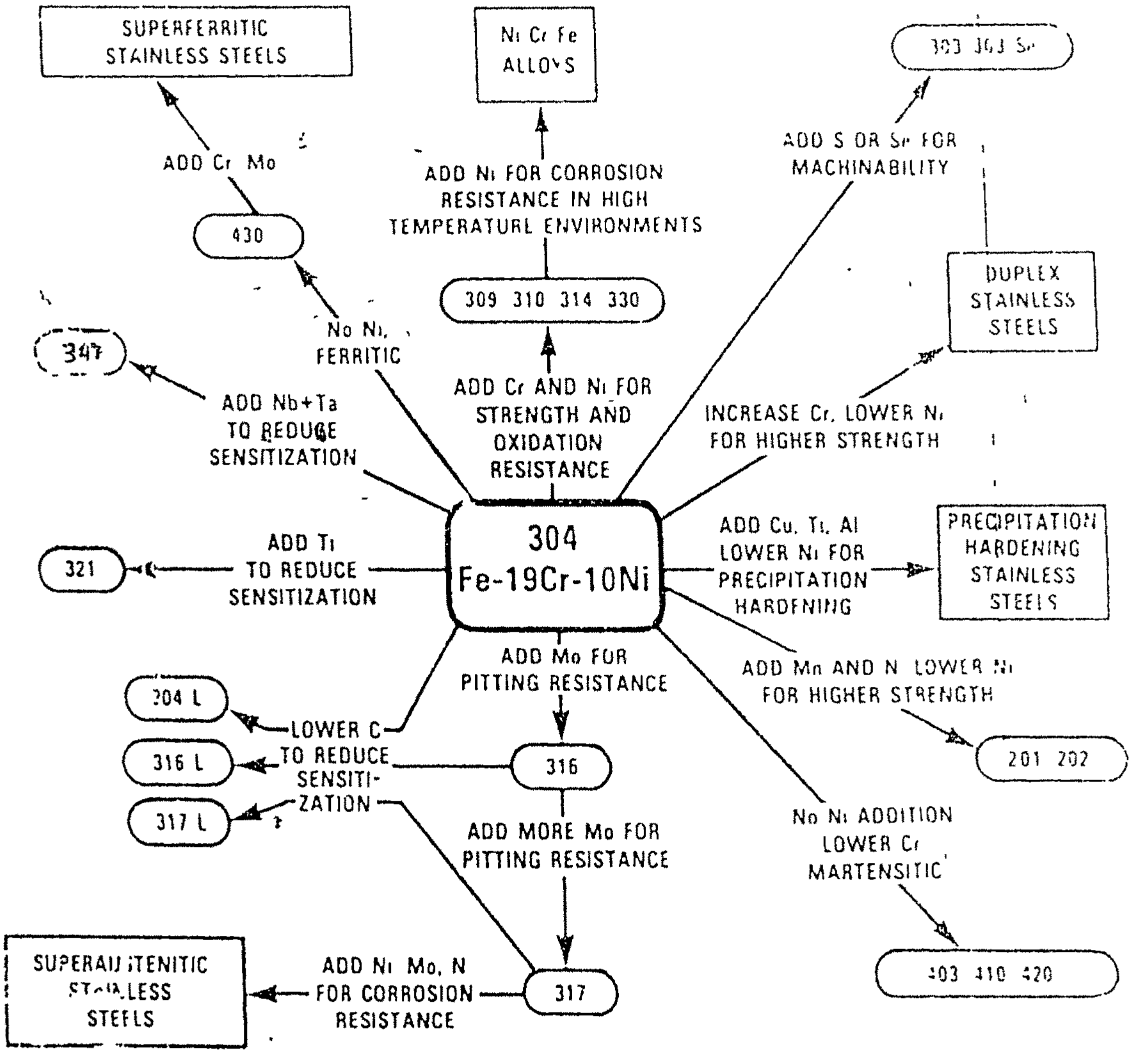


TABLE 2.1 PROPERTY LINKAGES IN THE SS FAMILY OF ALLOYS.

Types 305 and 384: These types have higher nickel contents, exhibit low wok hardening rates and are used in application where cold formability is important. Type 302 contains copper, exhibits work hardening rates even lower than those of types 305 and 384. It can facilitate sever cold working and is used for wire. Type 304 is used for welding rods.

Types 309, 310, 314 and 330 have higher nickel and chromium content to provide oxidation resistance and creep strength at elevated temperatures. Types 309L and 310L are lower carbon versions used to minimize carbide precipitation near welds. Type 330 has a particularly high resistance to carbonization and thermal shock.

Type H grade ASS such as types 304H((530409), 316H(531609), 321H(53209), 347H(534709) and 348(534809) all have carbon contents greater then 0.04% and are used in the solution annealed condition. These precipitation ensure high and reproducible creep rupture strengths at elevated temp.

Type 316 contains molybdenum and has greater resistance to pitting in marine and chemical industry environments than type 304. For type 316, variations includes a low carbon grade (316L), a nitrogen containing grades for increased strength (316N), and a higher sulphur grade for improved machinability (316S), as well as the higher carbon grade 316H contains carbon greater than 0.04% and are used in the solution annealed condition.

In types 316LN and 304LN, the loss in strength resulting from lowering of the carbon content is compensated by addition of the strengthening element nitrogen. The resulting stainless steels are nitrogen-strengthened L grades that are resistant to sensitization since nitrogen used at the very low levels (0.10 - 0.16%) does not produce sensitization in ASS. In the nuclear grade (NG) variants of types 316LN and 304LN, which have been used for boiling water nuclear reactor piping, the carbon content is kept below 0.02% (max), which is below the 0.03%(max) carbon specified for types 304Ln and 316LN.

An extra high nitrogen grade 316L(Hi) N (S 31654) is also available with 0.16 - 0.30% nitrogen. Type 315 is a low molybdenum (1.25 -1.75% Mo) grade used for sheet and strip. **Type 317** contains higher level of molybdenum than type 316 and is therefore incrementally more resistant to pitting and crevice corrosion. Type 317L is the low carbon grade containing higher levels of molybdenum and nitrogen than type 317 for even greater resistance to pitting and crevice corrosion. **Type 321,347 and 348** are grades stabilized with titanium, niobium plus tantalum, and niobium, respectively for application requiring welded structures or for elevated temperature service. Type 348 is SS for nuclear used with restricted tantalum and cobalt content.

2.2.4 ROLE OF ALLOYING ELEMENTS ON CORROSION BEHAVIOR

CHROMIUM (Cr) is the element essential in forming the passive film on surface of the steel in presence of oxygenated substances, rendering it stainless characteristics. Other elements can influence the effectiveness of Cr in forming or maintaining the film, but no other element by itself can form the film. Although passivity is attained in the steels with 3-4% Cr, but neither the film is observed nor it much affective. The film is first observed at about 10.5% Cr, but is mildly protective, passivity sharply increases at11.5 to12% Cr. In simple word, in a mono atomic layer of 8 atoms one-chromium atom is enough for covering the layer by a film. In the range of 17 - 20 % and up to 29 %Cr increases film stability as well as corrosion resistance, but adversely effects mechanical properties, fabricability or applicability therefore it is often advisable to alter other elements with or without some increase in Cr.

Chromium (Cr) is a ferrite former or stabilizer, as it tends to suppress the ferrite - austenite transformation observed during heating of steel. Cr is easy to passivate than Fe and has low passivation current density (18). Chromium addition to plain carbon steel, therefore, facilitates passivation and effect increases with chromium content, as shown in figures-2.2. It has been described that at a negative (low) range of potential stainless steel becomes active in acid. As chromium could exist in unstable state of valence of 2, due to lack of sufficient O_2 and favors reductive dissolution of passive film. Increasing potential (oxygen potential of environment) to intermediate values, chromium assumes valence state of 3, which is cited as most stable state. And steel passes in to passive state. At still higher potential range chromium acquire 6-valence state, which readily form soluble compound (chromic acid). Stainless steel again become active and enters into trans-passive region. Thus, a small variation in composition of the steel affect the upper and lower potential limits defining safe intermediate range. A composition of steel best suited to withstand oxidizing acids is quite different from that most suited for non-oxidizing acids. In austenitic stainless steels it also effect the amount of nickel needed to ensure fully austenitic structure at room temperature.

Nickel is present as austenitic stabilizer, it reduces melting point of steel (~9 ^{0}C per 1%Ni) thereby improves its castability. Being austenitic stabilizer, it improves ductility at the expense of strength up to 15%, beyond this amount, it increases stacking-fault energy and restrict dislocation movement resulting in reduction of tendency to deform. Thereby decreases deformability and improves strength. Increasing Ni to 8-10 % lowers resistance to Stress corrosion cracking but further increase Ni restores resistance. Ni favors E_{pp} decrement and active range decreases with Cr as shown in figure 2.6 (19).

Nickel present in austenitic stainless steels, does not readily enter the oxide phase (20). Thus during the initial stages of metal dissolution plus film formation, Ni must be getting enriched on the metal surface, just below the oxide film. These minute areas are occurring at various discontinuities in the film, like inaccessible fine size fissures, pinholes and hair-cracks acting as cathode on which preferential O_2 reduction readily occurs, preventing reduction of stable oxide/s in the passive film. Hence presence of Ni enhances corrosion resistance of A.S.S. by favoring passage into passive state. Moreover, Ni is effective in repassivation particularly in reducing environments. This is due to the fact that, chemical reactions, like reductive dissolution of passive-oxide film and cathodic reduction of O_2. In presence of Ni, exposed surface areas at the bottom of these discontinuities become more passive and favoring O_2 reduction, which may be present in very a small amount, rather than reductive dissolution of oxide-film. Such an action of Ni is revealed from the fact that, with increasing Ni-content in steel, its passive range increases.

Although nickel increases corrosion resistance, through making the steel surfaces more passive. Its addition must be balanced, as higher amounts affect the mechanical and other properties of austenitic stainless steels. Of course with chromium content above about 18%, amounts of nickel require for ensuring austenitic phase at room temperature, will increase. Also nickel reduces the tendency of sigma-phase formation, a phase considered to be deleterious for both mechanical and corrosion properties. Other intermediate phases; chi, luaves, gamma prime etc. do form in common austenitic steels and changes their properties, are also affected by nickel in presence of other alloying elements and specific conditions.

MOLYBDENUM (Mo) as an alloying element has following principal functions, with respect to corrosion behavior of austenitic stainless steels. Molybdenum is ferrite stabilizer. Hence need " balancing" in compositions to get austenite and avoid formation of detrimental phases like chi and sigma, during holding or slow cooling through temperature range 750-870 °C. Increasing Ni and reducing Cr content of the steels commonly achieve this "balanced", as seen in compositions of steels type 304 & 316.

In combination with Cr it is very effective in terms of stabilizing the passive film in the presence of chlorides, avoiding initiation of pitting or localized form of attack. It imparts high temperature strength, tensile and creep strength. It increases acid resistance without affecting heat weldability; treatment effects as graphitization, temper embrittlement are reduced. Molybdenum bearing steels are well suited to applications in variety of acids, such as sulfuric, phosphoric and hydrochloric from dilute to moderate range (21).

Passivity behavior of austenitic stainless steel containing molybdenum and chromium can be understood using simple assumptions. The most active component of alloy assumes to be the donor element and share the electron/s with acceptor element, which absorbed the electron/s and assume to be passive component. In austenitic stainless steel, accordingly, iron atoms fill the d-electron vacancies of chromium (22,23). Up to the critical composition at which vacancies of Cr are filled, i.e., less than 11.5%Cr, alloy behaves like that of iron. Beyond this value of chromium, the d-electron vacancies of Cr are unfilled, and alloy behaves more like chromium. In the ternary Fe-Cr-Ni solid solution mostly Ni above 50% donates electrons to Cr but by iron in lower nickel content (24). Similarly in type 316steel, alloys retain large part of the useful corrosion resistance of molybdenum so long as its d-band energy levels remain unfilled. Here again Ni donates electrons up to critical value 85%, as was found in binary alloy Ni-Mo for best corrosion behavior. Thus, steel type 316 will act like Mo so far as ratio of Mo/Ni is maintained at or above 15/85, at or above this ratio, passivity imparted by Mo appears to be optimum (25). **CARBON (C)** permits hardenability and high temperature strength but is detriments to corrosion resistance through its reaction with Cr, as it leads to Intergranular corrosion when under susceptible condition Carbon is also extremely to toughness.

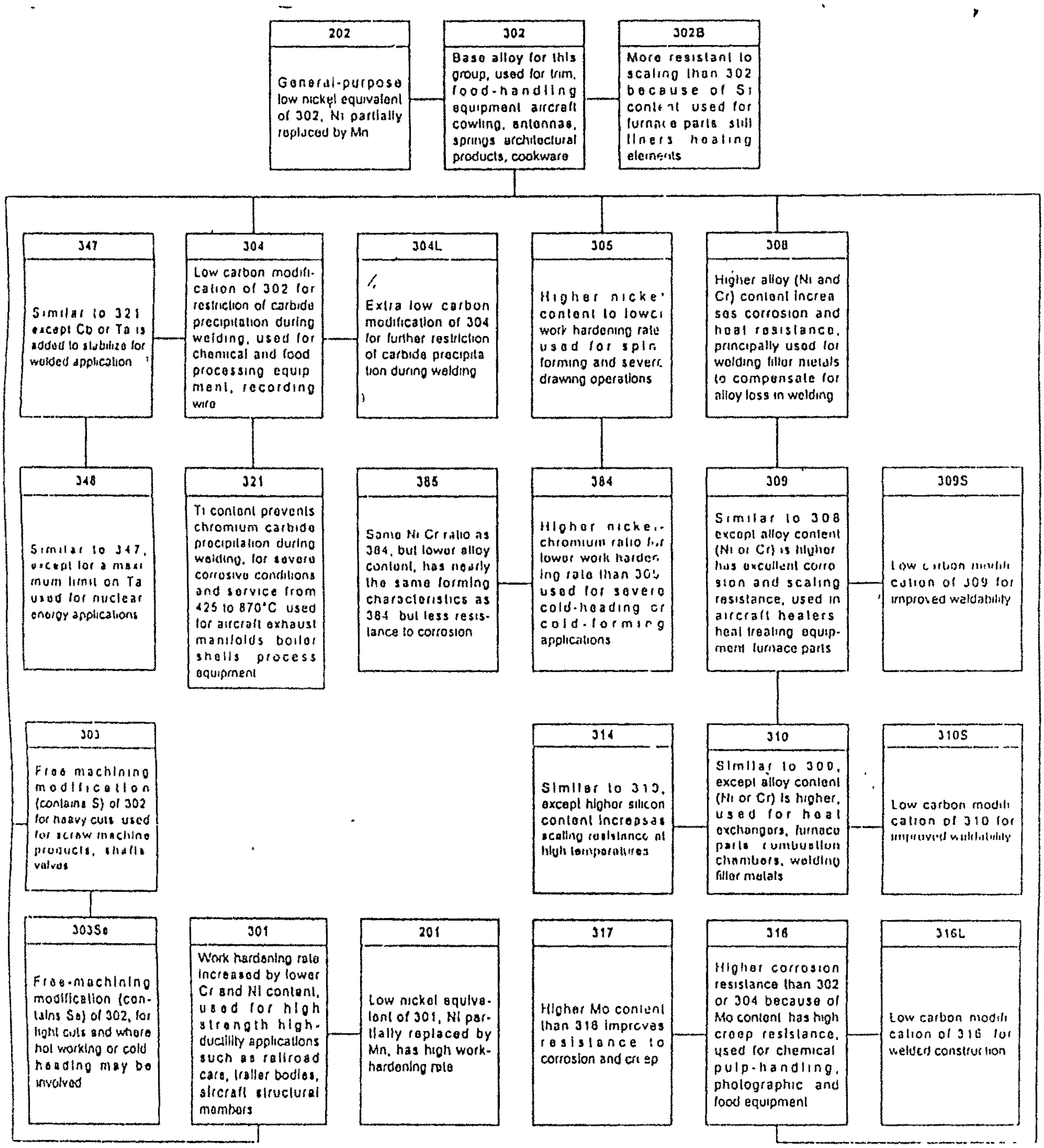
MANGANESE (Mn) being an Austenite stabilizer can replace Ni to a certain extent.

However complete replacement of Ni is not possible. High Mn steels have resistance to galling, forms sulphide whose composition and morphology have substantial effects on corrosion resistance, especially pitting.

NITROGEN (N) enhances pitting resistance in ASS retards a phase formation, reduces segregation of Cr - Mo.

SULPHUR (S) improves the machinability.

SILICON (Si) improves oxidation resistance. It is added intentionally to provide high temperature resistance.



Specific applications of different grades of austenitic stainless steels
(Source Lincoln Handbook)

COMPOSITION OF REPRESENTATIVE STANDARD STAINLESS STEEL

TUNGSTEN (W) like Mo is resistance to non-oxidizing acid and localized corrosion.

. **NIOBIUM & TANTALUM (Nb & Ta),** These are used as stabilizing elements to tie up carbon and prevent intergrainular corrosion. They also promote high temperature strength through solid solution and precipitation hardening mechanism.

ALUMINUM & TITANIUM (Al & Ti), these are used in minor amounts as deoxidants to tic down carbon and nitrogen and also provide age hardening system for low and high temperature services. Al forms alumina scale and resist oxidation, carbonization and chlorination.

COBALT (Co), its high cost and low availability limits its applicability.

COPPER (Cu) improves acid resistance and strength. Cu reduces corrosion current and retains passivity in reducing environment (26). It facilitates cathodic reaction thus raising cathodic current in passive range.

2.2.5 Application of Austenitic Stainless Steel:

The austenitic stainless steel is widely used in the various commercial forms such as plate, flat, angle, channel, round bar, square bar, pipe etc. The 304 and 316 ASS are most popular materials for high strength and excellent corrosion resistance over wide range of temp. The major product manufacturing from Austenitic steels are as follows.

(1) Heat exchangers (2) Pressure Vessel (3) Agitator

(4) Reaction Vessel (5) Reboiler (6) Crystallizer

and many more.

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