SENSITIZATION IN AUSTENITIC STAINLESS STEELS DURING WELDING

by
M. N. PATEL and S. K. AGRAWAL
Metallurgical Engineering Department, Faculty of Technology & Engineering,
M. S. University of Baroda, Baroda - 1

INTRODUCTION

Austenitic Stainless Steels are characterised by high content of chromium (18-20%) and nickel (8-14%) present in the solution and which impart the characteristic corrosion resistance property to this variety of steel.

Chromium forms a continuous protective chromium oxide film and nickel help to stabilize the film. The minimum chromium content required for the formation of continuous stable film is 12%.

Now if the steel is exposed to a temperature range 450-925°C, chromium carbide precipitates at the grain boundary area. These decrease in chromium content in the area adjacent to grain boundary below 12% and major loss of resistance to corrosion is observed.

Sensitization can be defined as a precipitation reaction. in which chromium and carbon combined together at or adjacent to the grain boundary and forms $Cr_{23}C_6$ within a temperature range of 450-925°C.

In the weld structure due to sensitization, Intergranular corrosion takes place at some distance away from fusion line in the heat affected zone. This phenomenon is called WELD DECAY.

Similarly, corrosion occurs in a stabilised stainless steel due to high temperature in HAZ close to the fusion line. Such corrosion is known as 'KNIFE LINE ATTACK'. The high temperature causes Niobium and Titanium carbides to dissolve in the solution and the structure will be sensitized further on reheating or stress relieving in the sensitization temperature range.

Basic Mechanism of Sensitization

When the metal is heated in a sensitization temperature range or slowly cooled, due to difference in diffusion rates of chromium and carbon and since carbon being smaller in size is more mobile. Thus carbon atom diffuses towards Grain Boundary where it combines with chromium and forms $Cr_{23}C_6$ resulting in decrease in the content of chromium in the solution below 12% and in the vicinity of the grain boundary is shown in Fig.1. The decrease in chromium content below 12% leads to discontinuity in the protective chromium oxide

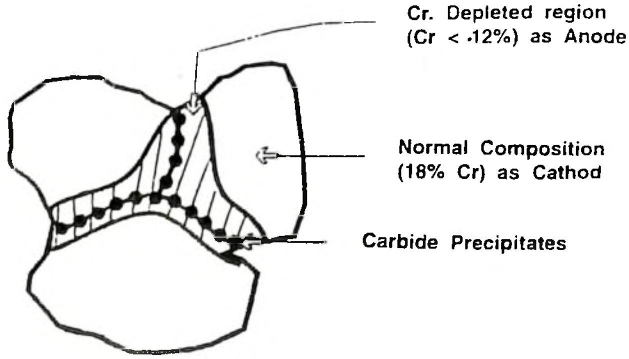

Fig.1 : Grain Boundary in 316L Sensitized Stainless Steel

film, which means a danger of Intergranular corrosion if exposed to a corrosive environment. These chromium carbide precipitates act as cathodic to the surrounding area, which gets preferentially attacked.

The depletion of chromium can be shown in Fig.2.

Sensitization can occur in two ways

1) Isothermal Heating :
   During heat treatment in the sensitization temperature range.
2) Continuous Cooling :
   Sensitization occurring in the welded specimen.

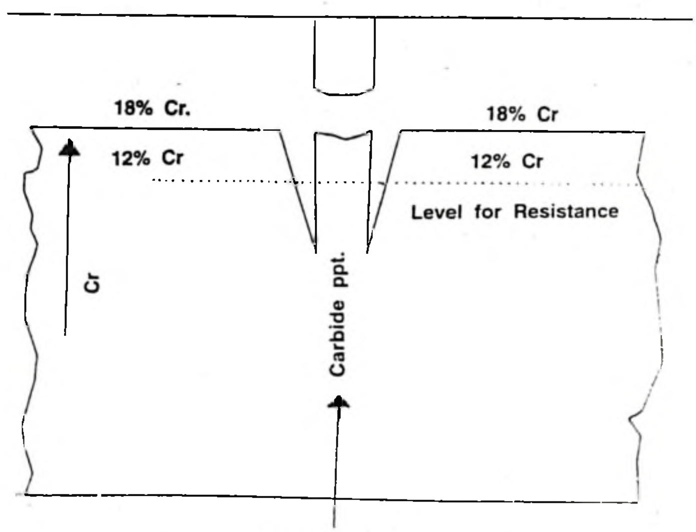

Fig.2 : Distribution of Cr in Vicinity of Carbide Particle

Carbide Morphology

As shown in Fig.3, carbides precipitate first on the delta ferrite - Austenitic interface, then on the grain boundaries, later on the incoherent twin boundaries and finally on coherent twin boundaries. There is a direct correspondence between corrosion behaviour and morphology of grain boundary carbide i.e. poor intergranular corrosion resistance is associated with sheets of connected small particles and good resistance with isolated dendritic particles.

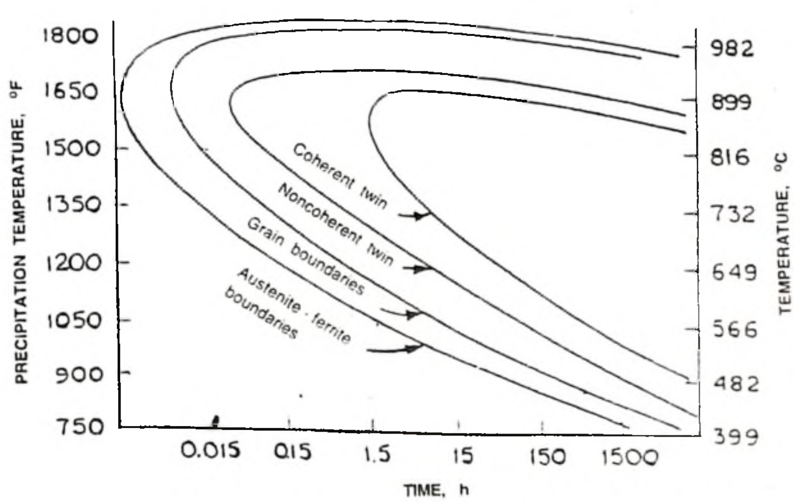

Fig.3 : Precipitation Kinetics of $M_{23}C_6$

Theories of Sensitization

There have been essentially three models proposed for intergranular corrosion of sensitized austenitic stainless steel.

a) Chromium Depletion Theory
b) Noble Carbide Theory
c) Seggregation Theory

Chromium Depletion Theory

This is a universally accepted one. It was proposed by Bain. This theory attributes to the depletion of chromium content in the region adjacent to the grain boundary to the level below required for passivation. This theory is based upon the following assumptions.

- A minimum chromium content is required to form a protective passive film.

- The carbide precipitates contain about 75-90% chromium by weight percent whereas bulk alloy containing only 18-20%. Thus the surrounding matrix is depleted in chromium.
- During sensitization, the bulk diffusion of chromium from the matrix to the depleted region along the grain boundary is too slow to replace the chromium content.
- If the chromium content in the depleted zone is less than the minimum chromium level (about 12-13%) the passive film will not form.

Noble Carbide Theory :

This theory has been described by Sticker & Vicker. They proposed that corrosion was an electro-chemical reaction between the carbide particles and the matrix and proceeds rapidly along the grain boundaries where there is continuous path provided by connected carbide particles. This is an invalid theory to explain sensitization.

Seggregation Theory

According to this theory, the element seggregated at grain boundaries result in chemical difference between the boundary and matrix and this serves as the driving force for intergranular corrosion.

Factors affecting sensitization

1) Time of exposure
2) Temperature
3) Cooling rate
4) Alloy composition (Mainly C & N2)
5) Degree of Deformation
6) Grain Boundary Structure

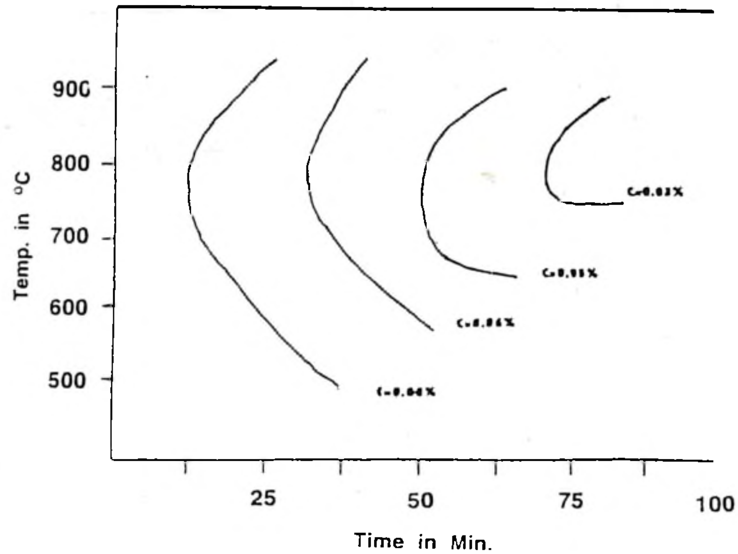

Fig.4 : Relationship between Temperature and Time

The effect of time, temperature and composition

As shown in Fig.4, time required for formation of carbide precipitation in stainless steel 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 steel with 0.05% carbon would be quite free from grain boundary precipitation.

Effect of alloying elements on sensitization :

Nitrogen : Nitrogen provides high resistance to intergranular stress corrosion cracking, it acts to retard the nucleation and/or growth of carbide at grain boundaries and hence increases the time necessary for sensitization.

Molybdenum :

- It increases time required for sensitization.
- It can eliminate possible detrimental effect of martensite on sensitization
- It accelerates phosphorus induced intergranular attack in Huey's test.
- Sigma phase formation is there which may render alloy susceptible to intergranular attack in certain oxidising media as well as severely embrittle the alloy.

Phosphorus

- Phosphorus decreases the corrosion resistance of Austenitic stainless steel
- Exact mechanism is not known.

Nickel : Susceptibility to sensitization increases with increasing nickel content.

Effect of Cold Work on Sensitization

With a small amount of cold work, a large increase in the dislocation density in the grain boundary region results in ease of precipitation and growth of carbides at the grain boundary when the cold worked material is heated in to the sensitization range. At the same time, the chromium diffusion rate in the bulk would remain unchanged and this would lead to severe chromium depletion in the vicinity of carbide network. With a larger degree cold work, the fact that Austenitic stainless steels are low stacking fault energy materials become important. Because of this increase in amount of cold work results in progressive layer dislocation pileups on slip planes. So, the carbide precipitation process increasingly favours nucleation site along slip planes. This would shorten the diffusion path for chromium and thus quicker homogenization of the chromium content in the matrix between bands of precipitated carbide within the grains.

Effect of Grain size

In fine grained structure the grain boundary density increases and hence, the nucleation sites for carbides are increased, thus susceptibility to sensitization increases.

STANDARD ASTM PRACTICES FOR DETECTING SUSCEPTIBILITY TO THE INTER GRANULAR ATTACK IN STAINLESS STEEL.

ASTM A262 practices

According to ASTM A 262 1970, recommended practices for detecting susceptibility to intergranular attack in stainless steel are as follows:

Practice A :
10% oxalic acid, Electrolyte etching at ambient temperature

Practice B : Boiling 50% H_2SO_4 + 25 g/l $Fe_2(SO_4)_3$

Practice C : Boiling HNO_3

Practice D :
10% HNO_3 + 3% HF at 70.

Practice E : Boiling 16wt % H_2SO_4 + 5.7% $CuSO_4$ + metallic Cu

Oxalic Acid etch test (ASTM A 262A)

This is rapid method for classification of standard structure of austenitic stainless steels by simple etching. The austenitic stainless steels which are essentially free from susceptibility to intergranular attack associated with chromium carbide precipitation have low corrosion rates in certain tests and therefore can be screened from testing as acceptable. (This test is used for acceptance of material but not for rejection).

The specimen after polishing upto 1u finish on 3/0 emery paper is anodically polarized 1.5 minute at 1 A/cm² at room temperature in a solution prepared by dissolving 100 gms of $H_2C_2O_4 . 2H_2O$ in 900ml of distilled water. Then surface is examined at 500x to classify structure as step, ditch or dual.

Step Structure : Immune to intergranular attack and no further testing in necessary.

Ditch Structure : Further test by Huey's test or some other test viz Practice B to E.

Dual Structure : Further test necessary.

Ferric Sulphate - Sulphuric Acid Test (ASTM A 262B)

This practice suggests 120 hours exposure of specimen for boiling of 50 wt% H_2SO_4 + 25g/l $Fe_2(SO_4)_3$ and assessment is done on weight loss basis i.e.

$$\text{Ratio } R = \frac{\text{wt. loss of sample to be assessed}}{\text{wt. loss of annealed sample}}$$

R> 1.25 - 2 indicates susceptibility. Several specimen can be tested in the same solution and it is twice as fast as Huey's Test.

Boiling HNO_3 Test or Huey Test (ASTM A 262 - C)

Here specimens are exposed in fresh boiling 65% HNO_3 for 5 successive periods of 48 hours each. The specimens are cleaned and weighed after each period of test and corrosion rate (penetration rates) is calculated and is averaged over the 5 periods expressed in inches per month (ipm).

This test gives high corrosion rate and is valuable for evaluating alloys for use in HNO_3 or in other strongly oxidizing acid solution. Since most service conditions do not cause attack on alloy in these conditions the test can be misleading.

HNO_3 - HF Test (ASTM A 262 -D)

This test consists of two hour periods for each period in 10% HNO_3 + 3% HF solution at 70°C using fresh solution for each period. Intergranular attack is assessed by penetration rate evaluated from weight loss if greater than 1.5 times that of standard. The former is considered to be susceptible.

This test is more rapid than the other tests and is specific for chromium carbide precipitation. It gives constant and reliable results. Main disadvantages are the need of using a ratio of two test rates and inconvenience of handling the solution containing HF.

Copper - Copper Sulphate 10% H_2SO_4 Test (ASTM A262 E)

Also called STRAUSS test consists of dissolving 100 gm of copper sulphate in 700 ml of sulphuric acid and diluted by 1000 ml distilled water. Electrolytic grade copper shots are used to cover the specimen. Minimum time of test is 24 hours. Evaluate the results qualitatively by bending the specimen around a mandrel through 180°C and inspecting bend for cracking.

Copper chips are placed in contact with the specimen to speed up test and decrease testing time (rate of intergranular attack increases as copper decreases the corrosion potential of stainless steel).

Disadvantages of ASTM A 262 practices

1. ASTM practices do not readily qualify degree of sensibility
2. They are not rapid (with exception of 262 A)
3. They are destructive. ■