Problems in Welding of High Temperature Alloys in the Fertilizer Industry

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Introduction

The Naptha/Steam Reforming Process for the production of synthesis gas required for ammonia in the fertilizer industry has necessitated the use of materials which could retain their physical properties at temperatures as high as 950 to 1000°C and pressures of 12-15 kg/cm^2.

These materials have to be suitable for fabrication at shop level as well as in field and then operate under high temperatures and pressures. The materials are in service continuously for the flow of hydrogen and a mixture of hydrogen, steam, CO and CO_2 gases. In any unforeseen breakdown, the materials are subjected to thermal shocks and they are also liable to be subjected to high rates of cooling as the temperature of the system comes down very rapidly. In the following discussion, unless otherwise stated, the term "High Temperature" which has been frequently used, will mean temperatures above 500°C.

Materials Used

The materials used in the fertilizer industry can be classified as per their service viz.

(1) To stand high temperature and high pressure in the production of ammonia synthesis gas. Here corrosive environment is not the deciding factor. High temperature and mechanical properties of the material are the main design criteria and

(2) To stand highly corrosive atmosphere for the production of Urea and other phosphatic fertilizers. Here resistance to corrosion is of prime importance and not mechanical properties at high temperature.

Any corrosion or crack in the welding of stainless steel or alloy steel in urea or phosphatic fertilizer atmosphere or any other salt plant can be repaired without much of trouble. This paper is confined to stainless and high alloy steels used in ammonia plants for high temperature and high pressure services since these pose problems when repair welding is undertaken.

In the beginning, wrought austenitic steels were in use but the trend towards higher temperature and pressure necessitated developing nickel based alloys, because they have higher creep strength than wrought austenitic steels. The alloys developed had to possess higher strength than wrought austenitic steels and also better high temperature oxidation resistance.

Centrifugally cast high carbon austenitic steels appeared to be more suitable than wrought steels because of these requirements. Further, because of ease and simplicity in the manufacturing process, the centrifugally cast tubes were cheaper.

Welding of Alloy Steels

Important factors involved in the welding of alloy steels are :—

(1) The parent metal immediately adjacent to the molten pool is subjected to a high temperature

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thermal cycle accompanied by thermal strain, which may change its mechanical properties.

(2) A field of residual stress in the vicinity of weld remains associated with the joint after it has cooled.

(3) Design of weld joint and shape of bead often cause local stress concentration in the system.

(4) Weld metal has a different metallurgical structure from its surrounding material. It is possible that it may have a different chemical composition also.

Because of these four factors the performance of a welded structure is largely dependent upon the behaviour of welded details and not on the properties of unwelded parent metal. For an alloy to be perfectly weldable, the joints must be free of defects that might impair the mechanical performance.

All welding slag must be removed. The slag produced by nickel and high nickel alloy electrodes is not corrosive to the weld or base material, if the operating or service temperature is rather low. However, when service temperature approaches the melting point of the slag, severe attack can occur and since the temperature at which this attack will start cannot be accurately determined, it is necessary to ensure complete slag removal.

The joint design should be such that it helps the full potential of the parent material to be realised in service. The weld must completely penetrate or close the joint. This means no unfused areas should be left in any joint, particularly butt or fillet joints. If necessary, slight change in weld preparation may be made. In the case of a round or square joint, complete penetration may not be possible ; therefore, the weld should be continuous and completely seal the joint to eliminate penetration of carbon or processing material or exposure of hidden slag to oxygen rich atmosphere.

Corner joints should be avoided. Preference should be given to butt joints since here stresses act axially while in the case of corner or lap joints the stresses act eccentrically. A corner joint may cause early failure, if not supported properly. Where possible, the joint must be located away from corners even if slight modification in the design is necessary. If shifting of the joint is not possible, the weld must penetrate completely. If flow conditions permit and root side of weld is accessible, a backing weld may be used.

The term "weldability" in this case may be defined simply as the ability of the cast steel components to be joined satisfactorily by fusion welding e.g. tungsten-inert gas (TIG) or metal-arc flux-coated electrode process, without the occurrence of detrimental effects associated with gas porosity and, more particularly, cracking in the parent metal heat-affected zone. Apart from the intrinsic "weldability" of an alloy steel upon which, for instance, the distribution and quantity of its carbide phases as well as its ferrite content will have an essential influence, the feasibility of making a satisfactory welded joint depends also upon a number of factors which include :—

1. Type of restraint across weldment
2. Thickness of section to be welded
3. Welding process used, e.g. TIG or Metal-Arc and root run technique
4. Form of weld preparation
5. Grain size and
6. The quality of standard required and the inspection techniques employed.

Effect of Presence of Carbon, Silicon and Manganese on Weldability

While undertaking welding of new cast headers and Tees of 25/20/0.4 Cr/Ni/C, we have observed that this material has got good weldability property in as-cast form.

It is believed that a high carbon content confers improved weldability in such fully austenitic high alloy heat resisting steels due to a mechanism involving the "healing" of incipient micro-fissures by the relatively low melting point eutectic carbide phase that occurs in significant quantities in these types of steel in the "as-cast" condition.

On the other hand, this high carbon percentage in this material has been found to be undesirable so far as the weldability of this materials is concerned when the material has been once put in service. This appears to be the result of the precipitation of secondary carbides, partially as a product of the break-down of low melting point eutectic carbide phase. This phenomenon occurs at temperatures between the range of 600°C and 1100°C which is reached either due to service at high temperature or due to welding or due to heat treatment.

This precipitation results in increased strength and reduction in ductility but some loss in weldability, reflected in the fact that weld repairs of this material used in our hydrocarbon reforming plant tubes is substantially more difficult after they have been in service than in the case when the steel is in the "as-cast" condition.

When discussing the weldability of HK-40 (i.e. 25/20/0.4 Cr/Ni/C) there are two important points to be made.

1. Apart from the effect of Carbon, it has been observed that the production of satisfactory weldments in these types of steel also depends, in some measure, on maintaining the silicon content of both the weld and parent metal as low as possible. Experience dictates that the ratio of C : Si should not be less than 0.5. In this respect it is preferable to use TIG welding process because, in this case, we have greater tolerance for microfissuring, a hazard caused by silicon deposit.

Material of the tubes now available has a ratio C : Si of 0.2, much lower than what is desirable. New materials which are now expected to come in the market on a commercial basis have been developed bringing this ratio near 0.5. IN-519 an alloy which is in the development and observation stage at present is having better properties than HK-40 and this is having the ratio of C : Si equal to about 0.25.

2. The percentage of manganese has also been observed to be affecting this hazard of micro-fissuring, but in the reverse way to Silicon. It offsets this hazard in weld deposits although the extent to which this effect is obtained is limited by the normally specified maximum of 2% for this element. In IN-519 manganese has been reduced to only 50% of that of HK-40.

Conclusion

Both cast and wrought austenitic materials can be welded without apparent difficulty by manual, semi-automatic or automatic techniques using a number of filler compositions. The low carbon cast or wrought materials may contain micro-cracks that can be revealed by very detailed examination. Further, welds in most austenitic materials develop poor heat affected zone hot ductility on reheating. This can result in cracking. Micro-cracking in the heat affected zone occurs as a result of local melting of grain boundaries' constituents in the parent material immediately adjacent to the fusion boundary of the weld. The thermal strains accompanying welding may then open up these regions, before they solidify to form small cracks known as hot tears. They may occur both in low carbon cast materials and in wrought materials and have no appreciable effect on the tensile strength or ductility measured at low temperatures. However, they may provide nuclei from which cracking due to thermal fatigue or creep could propagate during the service life. In certain systems, they are known to initiate serious heat treatment cracking immediately after welding. Nearly all austenitic materials are susceptible in some degree to this problem including cast austenitic steel. However, whether it occurs in practice depends on a number of factors, such as the thickness of the material, the type of joint, composition of the steel, strength of the weld metal etc. There is the risk of such failure in both high and low carbon cast austenitic material, and it is important to determine the relative susceptibility of these materials to assess whether conditions, as they exist now or as they will exist with more advanced design, may lead to risk of practical cracking problems continuously in service.

If small micro-cracks exist in the heat affected zone such as hot tears, the likelihood of cracking is very much greater since the heat affected zone cracks will tend to propagate from the hot tears.

Repair Welding

The repair welding of high carbon cast austenitic materials is difficult if the component concerned has been in high temperature service. This is because the ductility of the parent material may have become so low that spontaneous cracking occurs near the weld under the influence of welding stresses.

The failure of reformer tubes is largely due to creep. It has been observed in these cases that though a large number of cracks develop in the material, only a few of them reach the surface of the material.

Creep failure in our experience is mostly due to local overheating as a result of catalyst damage or due to uneven heat distribution inside the furnace.

In almost all tubes used in our furnaces, bulging of the tube has been observed due to localised heat development.

The repair of cracks in these tubes is difficult because attempt to repair the crack by welding does help in propagating the crack to some adjacent point. This happens because material in the region of creep failure often contains a large number of both small and large cracks. All of these may not be visible on ordinary examination of the surface. When welding for the repair of the main crack is attempted, the other invisible cracks start appearing due to the development of welding stresses. Some of the cracks will get their lengths increased, some will reach upto the surface and some will come to the point when any subsequent welding will be sufficient to help them to appear at the surface.

Normally repair welding in such cases is not advisable. As an alternative, in some cases, if the length of the crack can be accurately determined by means of X-Ray or Gamma-Ray Radiography, the complete damaged section of the piping can be replaced with new material if the crack is not very long.

The other reason why new cracks start developing when repair welding is done may be due to the appearance of sigma phase in HK 40 alloy. Sigma phase causes brittleness of the steel at temperatures below 200°C. If the tube material contains much sigma phase, welding will become very difficult. Crack development in parent metal is found due to the extremely brittle metallurgical structure of the material.

HK-40 is liable to suffer from carbide precipitation during ageing at service temperature which in turn contributes towards embrittlement of this material after service.

It can be seen that most of the trouble which was experienced during welding was due to brittleness of the parent metal at room temperature. Therefore, for success in welding repair, it is of immense help to keep the strain produced in the parent metal during welding to its minimum. This may be accomplished by the deposition of small weld beads incorporating a very small amount of weave and allowing the joint to cool down between passes. Nickel based consumables are useful in reducing the risk of cracking in the parent material.

The problem of failure of tubes and subsequent repairs has been discussed with experts and specialists in this field in the U.K. and elsewhere. They say that merely repairing the crack is not sufficient in the existing case as although the areas in the vicinity of the crack are leak-proof at the testing time, they all are in an advanced stage of creep and as such they are not expected to give a reasonable life during service. Repair welding is not, therefore, recommended.

The material of tubes and headers used in our plant is HK-40 alloy centrifugally cast while the fittings such as elbows, tees and flanges are static cast. The material of pipes connecting reformer tubes to header is Incoloy alloy 800. The compositions of these two alloys are as given in the table.

The repair welding on the centrifugally cast HK alloy tubes and wrought Incoloy pipes has been in most cases, by tungsten-inert-gas (TIG) process. The electrodes used have been type 310 coated electrodes, and filler rods type Inconel 82. The currents used were in the range of 100 to 125 amps. depending upon the thickness of the section.

Although the repair of cracked tubes is not recommended as discussed earlier, in the absence of spares, repair has been tried and successfully also. This happened in December, 1967, when a number of tubes on different assemblies cracked in our reformers. Four such assemblies, two comprising six tubes each and two eight tubes each had to be changed since no repair on the cracked tubes could be attempted, because of big openings as a result of bursting of tubes. The problem of crack propagating was experienced while doing repairs on other tubes, but continuous trials proved successful.

Three tubes on one assembly of eight tubes and one tube on one assembly of six tubes were repaired successfully by TIG process, using Inconel 82 filler rods. Out of these two assemblies the latter gave successful performance from December 1967 to May

TABLE

Name of Material	*Alloy Type*	*ASTM Specification*	*Nearest AISI Type*	*Chemical Composition*					
				Ni	*Cr*	*C Max*	*Mn Max*	*Si Max*	*Mo Max*
HK-40 (Casting)	25 Cr-20 Ni	A—297	310	20	25	.4	2	2	.5
Incoloy Alloy 800	35 Cr-30 Ni	B—407		35	23	.1	1.5	1	—

1969 when the plant was shut-down for annual maintenance. The leak on the repaired portion was noticed only when the furnace had been cooled and a test was done pneumatically. Since in he hot condition while in operation, this leak was not observed, it may be presumed that this might have occurred while cooling. An attempt was made to repair this, but it was not successful and the complete assembly had to be changed.

The three tubes repaired on the other assembly were found all right and these are again in operation since June 1969.

It may be of interest to mention here that repair on one pipe header joint (centrifugally cast pipe) with a static cast tee was not successful even after persistent trials by TIG process using bare 310 filler rod. Then a trial was made using coated electrode of 310 type by arc welding and it proved successful.

Although the root pass and other subsequent passes can be done using coated electrodes, it is preferable to use the TIG process for the root pass with or without filler rod and then use coated electrodes for subsequent passes, in order to avoid cracking tendencies.

For complete joints filler rods and tungsten inert gas process were used.

Another place of great difficulty in repair welding has been a tee (on the main header) joint to a cone (leading to one waste heat exchanger). Both tee and cone are static cast and there is no difficulty while welding new pieces. But, after the pieces have been in service, welding cracks have been observed after every cooling of the joint. This is probably because of direction and velocity changes, but to discuss it here is beyond the scope of this paper. While repairing, the phenomenon of crack propagation has been observed frequently. Repair could be done successfully when the cracks were attended one by one on opposite sides of the joint, so that the tension developed while cooling equalizes.