Estimation of Delta Ferrite in Austenitic Stainless Steel Weldments by an Electrochemical Technique

The absolute content of delta ferrite is determined by preferentially dissolving the austenite phase and then estimating the undissolved ferrite gravimetrically.

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ABSTRACT. An electrochemical technique was developed to estimate the absolute content of delta ferrite in austenitic stainless steel weldments by preferentially dissolving the austenite phase and keeping the ferrite phase passivated. The undissolved ferrite was separated and estimated gravimetrically. The estimation of the ferrite by this technique, when compared with optical and magnetic methods, showed slightly lower values.

The morphology of the delta ferrite was studied with a scanning electron microscope after partially dissolving the austenite. The micrographs obtained indicated clearly a three-dimensional network of the ferrite. The separated ferrite was compacted and its polarization behavior studied. The elemental analysis of the ferrite was also carried out using an electron probe microanalyzer.

Introduction

The presence of delta ferrite above a certain level in austenitic stainless steel weldments renders them less susceptible to microfissuring and hot cracking. Delta ferrite is also beneficial in increasing the strength and in improving the corrosion resistance; however, there is a reduction in ductility and toughness. Ferrite content above a certain level is unacceptable for welds meant for high temperature service because the creep-rupture properties are adversely affected. Therefore, for many applications involving high temperatures, it is required to specify the ferrite content of the weldment in the narrow range of 2 to 6 Ferrite Numbers (FN).

Techniques and standard procedures for measuring ferrite levels to the required accuracy have not been available so far. The magnetic (probe), X-ray diffraction, and metallographic methods make only surface or limited volume measurements. Schaeffler and Delong diagrams can also be used for the measurement of ferrite if the chemical composition of the weld deposit is known. But the accuracy of such a measurement is only 3 to 4%.

The magnetic saturation method, which involves determining the permeability of the weld specimen at saturation is an accurate method for measuring the absolute ferrite content of the weld. However, it is complex and involves a number of assumptions and calculations regarding the chemical composition of the ferrite. Another possible method involves the use of Mössbauer effect measurements. However this is still in a developing stage and will estimate only highly localized ferrite content.

This paper describes the attempts made to determine the absolute content of delta ferrite in the weldment by an electrochemical technique. The technique consists of exposing a sample from the weldment to an electrolyte at a certain fixed potential. At this critical potential the austenite of the duplex austeno-ferrite structure is selectively dissolved while the ferrite which becomes passive remains undisolved. The undissolved ferrite is collected and weighed.

Experimental Procedure and Results

At the outset, experiments were carried out to determine the anodic polarization diagram of a Type 316 stainless steel weldment (austenoferritic structure) in a de-aerated aqueous solution of 3.6 N sulphuric acid and 0.1 N ammonium thiocyanate contained in a polarization cell assembly shown in Fig. 1. Oxygen-free dry argon gas was bubbled throughout the test period. Specimens polished with up to 600 grit emery paper and platinized platinum auxiliary electrodes were introduced into the solution after one hour of argon bubbling. The steady state potential was recorded 1 hour (h) after immersion of the specimen and then the anodic polarization was carried out in steps of 50 mV per 5 minutes (min) using a Wenking Potentiostat (model ST 72). The polarization curve thus obtained for the duplex steel is shown in Fig. 2.

The polarization curve for pure austenite was also similarly obtained. For this purpose a sample of the weldment was solution-annealed at 1100 C (2012 F) for 1 h and subsequently air-cooled. The specimen was found to be nonmagnetic after the above treatment. The polarization diagram for such a sample is also shown in Fig. 2. From this curve it can be seen that the critical current for the passivation of austenite is obtained at -50 mV (SCE) and that at or just below -50mV, the austenite will dissolve at the maximum rate.

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Further experiments were then carried out to selectively dissolve austenite from the duplex structure. These samples were maintained potentiostatically at -80 mV. This potential, just below the passivation potential, was selected to make sure that the austenite does not become passive. As reported by Bathily, at the potential below the Flade potential and in the solution under test, the ferrite remains in passive state. It was observed that during the initial period, the current density remains quite high (about 45 mA/cm$^2$) and after some time becomes low (about 0.007 mA/cm$^2$) and remains constant, indicating that all of the austenite has been dissolved out and only ferrite in passive state is left. At this stage, the sample was removed.

On examination it was found that a porous mass was left behind. It was successively cleaned with an acid mixture (50% sulphuric and 5% nitric acid), with distilled water and finally with acetone to remove the black anodic reaction product formed on the surface of the residue. The X-ray diffraction pattern of this mass, which was magnetic in nature, showed it to be bcc. Therefore, it was concluded that only delta ferrite was left. This was dried, weighed and compacted. The anodic polarization curve for the compacted delta ferrite thus obtained is also shown in Fig. 2.

Comparing the polarization diagrams of pure austenite and pure delta ferrite (Fig. 2), it is confirmed that at -80 mV ferrite remains in passive state whereas austenite dissolves in active state at a maximum rate. During the process of selective dissolution of austenite at the above-mentioned conditions, it was observed that some of the ferrite particles got detached from the specimen and either settled down or remain suspended in the solution where they dissolve actively at their corrosion potential (-370 mV). Moreover, the collection of loose ferrite particles is difficult at the end of the process.

To overcome these difficulties, a special specimen holder was designed in which all the loose ferrite particles always remain in contact with the rest of the sample. A sketch of the sample holder is shown in Fig. 3. A permanent magnet, which can be easily removed when needed, is embedded right below the platinum disc anode (on which the specimen is placed) in an epoxy resin mold.

Following the method described above, it was possible to completely separate ferrite from the duplex structure. This was cleaned, dried, weighed and the ferrite content gravimetrically estimated. The results obtained on four weldments made with OKR-3U (Type 316) electrode are presented in Table 1; the ferrite contents evaluated by the magnetic probe method and by metallography (a typical photomicrograph is shown in Fig. 4) on the same weldment samples prior to carrying out the selective dissolution are also included in Table 1.

The ferrite residue of sample no. 2 was compacted and analyzed for Cr, Ni and Mo contents by electron probe microanalyzer. Table 2 shows the results of this analysis. This indicates the enrichment in Mo and Cr and depletion of Ni in the ferrite phase. With a view to studying the morphology of the delta ferrite, samples from the weldment, exposed for different lengths of time at the condition needed for the selective dissolution of austenite, were examined under a scanning electron microscope. Typical SEM micrographs are shown in Figs. 5 and 6.

Discussion

The electrochemical technique (ECT) for delta ferrite measurement can be a method for measuring the absolute content of delta ferrite, whereas optical and magnetic probe methods provide only surface and near-surface contents of the ferrite. Comparing the results with other methods as shown in Table 1, we find a lower value of delta ferrite by ECT.
This difference may be attributed to two factors.

1. As stated previously, this difference arises due to the fact that ECT gives true gravimetric content of the delta ferrite whereas by optical and magnetic probe methods only surface content of the delta ferrite is measured.

2. There is some loss of ferrite due to its dissolution at the very small current density in the passive state (0.007 mA/cm²) *.

The complete dissolution of austenite requires exposure of the sample for a long period which depends on the thickness of the specimen and its ferrite content. (For instance, a 1 mm (0.04 in.) thick specimen containing about 3% delta ferrite needed about 40 h for the complete dissolution of the austenite. The delta ferrite in its passive state is only 1% of the estimated ferrite content. (For instance, a 1 mm (0.04 in.) thick specimen containing about 3% delta ferrite needed about 40 h for the complete dissolution of the austenite phase). During this long period some loss of ferrite is bound to occur.

The error due to the second factor can be eliminated if a correction factor is applied with respect to the loss of ferrite in its passive state. Our calculation shows that maximum error introduced due to ferrite dissolution in this condition is only 1% of the estimated ferrite value.

The ECT may also be utilized for studying the morphology of delta ferrite after the austenite phase is removed from the structures. Figures 5 and 6 show the SEM photographs of delta ferrite network after two hours of selective dissolution. In Fig. 5, the microstructure of the interface of pure austenite and duplex structure reveals the uniform dissolution of austenite and selective dissolution of the duplex structure; in Fig. 6, the three-dimensional network is evident. The optical metallograph shown as Fig. 4 indicates that delta ferrite occurs as a discontinuous dispersion in the austenite matrix. The SEM pictures clearly establish that the ferrite phase forms a three-dimensional honeycomb network. The specimen of Fig. 6 was estimated to have 2.74 vol-% delta ferrite. This contradicts the earlier opinion* that the formation of such a honeycomb network of delta ferrite is likely only when the ferrite content is greater than 4 to 7 FN.

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**References**

The Aluminum Alloys Committee of the Welding Research Council... is pleased to announce that it will sponsor three important sessions on the welding of aluminum during the 61st Annual Meeting of the American Welding Society in Los Angeles, California, during April 14-18, 1980. The three sessions—each of unusual interest to metal fabricators working with aluminum—are:

- **Design of Welded Aluminum Structures**, on Tuesday afternoon, April 15—co-sponsored by the Aluminum Association and the AWS D1 Structural Welding Committee.

- **Aluminum Weldments—Part I**, on Wednesday morning, April 15. New process developments for application during the welding fabrication of aluminum and its alloys.

- **Aluminum Weldments—Part II**, on Wednesday afternoon, April 15. Research and development, with emphasis on the outcome of weld cracking studies.

Full details are contained in the tentative program for the 61st Annual Meeting technical sessions program that appears elsewhere in this issue of the *Welding Journal*. (See Table of Contents, page 3.)