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Prediction of embrittlement during aging of nuclear grade AISI 304 stainless steel TIG welds

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Simulated weldments of AISI grade 304 stainless steel having a ferrite content of 4–6% with three levels of nitrogen (0·03, 0·08, and 0·11 wt-%) were prepared using a modified elemental implant technique. From these weldments, subsize Charpy impact specimens were prepared and subjected to aging treatment at different temperatures, 623–748 K, and for different times, 1000–5000 h. Impact toughness curves for these aged samples were generated by testing at various temperatures from 77 K to 300 K. From the impact curves the upper shelf energy (USE) and lower shelf energy (LSE) were determined. It was observed that both USE and LSE decreased with aging time at all temperatures. Nitrogen seems to offer a beneficial effect as far as impact toughness is concerned, as both USE and LSE values increased with increasing nitrogen content. The worst aging conditions were identified as 748 K, 2000 h at the lowest nitrogen level of 0·03 wt-%. An empirical relation connecting the aging temperature, aging time, and nitrogen content to the LSE was developed, which can be used to predict the time for embrittlement at a given nitrogen level and aging temperature.

Keywords: Stainless steel, TIG welds, Aging, Charpy impact, Lower shelf energy, Embrittlement

Introduction

The AISI 300 series (austenitic stainless steels) is the largest group of stainless steels in use, as these alloys have high ductility, low yield strength, high tensile strength, are easily fabricated, and have excellent corrosion resistance.[1] Large tonnages of stainless steel structures are fabricated by welding in the nuclear and other industries; however, these materials are not designed primarily for weldability and there is a continuing need to investigate and solve problems faced during and after fabrication. Hot cracking and microfissuring due to the presence of impurity elements such as sulphur, phosphorus, and minor elements such as boron, silicon, and niobium often occur in stainless steel weldments.[2–4] This problem can be avoided by retaining about 4–6% of ferrite in these welds. However, the room temperature ferrite in the weld metal is a metastable phase, which transforms to various other phases on aging, thereby causing embrittlement of the weld.

Addition of nitrogen to stainless steels was found to be beneficial as it improves austenite stability, thereby reducing the nickel requirement and enhancing mechanical properties and corrosion resistance.[5]

The present work deals with investigations into the effect of nitrogen, aging temperature, and aging time on the impact behaviour of type 304 stainless steel TIG welds. Aging temperatures were chosen to correspond with service temperatures in nuclear reactors, where these steels are used. An attempt was made to predict embrittlement in these materials by developing an empirical relationship.

Experimental

Materials

Nuclear grade AISI 304 stainless steel plates with composition as given in Table 1 and of dimensions 200 × 100 × 12 mm were obtained from IGCAR, Kalpakkam, India.

Argon gas used for the experimental work was of commercial purity, obtained from a local gas agency. The elemental nickel, required to reduce the ferrite content in 304 SS welds, was used in the form of shots of 99·99% purity.

Equipment

TIG welding unit

A welding equipment TIG-400 (AC/DC), manufactured by M/s Mogora Cosmic Pvt. Ltd., Pune was used to simulate the weldments. An auto torch movement setup

Table 1 Chemical composition of the sample AISI 304 stainless steel

Element	C	Cr	Ni	S	Mn	N
wt-%	0·084	18·6	12·7	0·012	1·0	0·03

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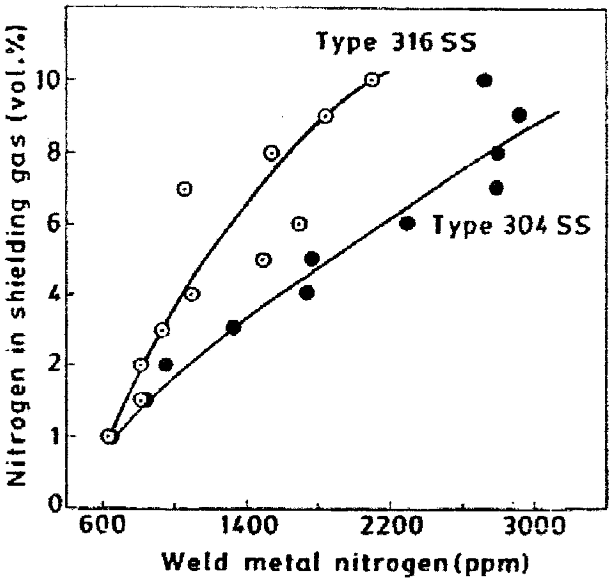


1 Solubility of nitrogen in weld metals of type 304 and 316 SS as a function of nitrogen gas mixed with shielding argon gas[6]

was fabricated and mounted on a rigid mild steel working table. The movement of the torch was controlled by a motor through a belt and wheel arrangement to give a torch speed of 6 cm min^{-1}.

Magne-gage ferrite tester

The ferrite content in the weld metal was determined in terms of ferrite number using a Magne-gage supplied by Magne-gage sales and services, Dorsey Mill Road, Glenwood, USA.

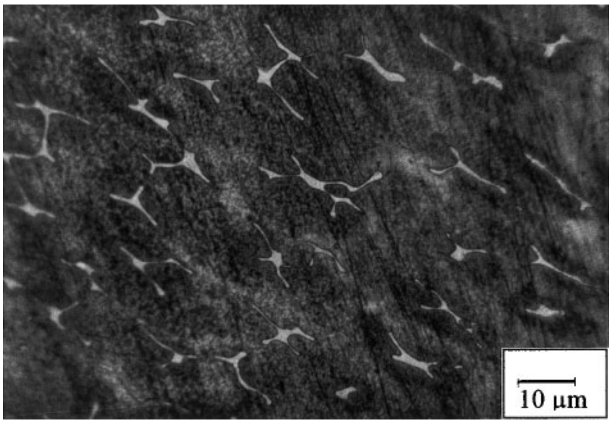
Furnaces

Electrical resistance muffle furnaces were used to age specimens. These furnaces were provided with thyrister type temperature controllers with an accuracy of ± 1 K, and provided a maximum temperature of 1273 K. Each furnace was connected to a timer to record aging time.

Impact testing machines

The room temperature impact values of welded and aged specimens were determined using a Charpy impact tester of Russian make, MK-30A with a capacity of 300 J.

The subzero impact values were obtained using a Tinius Olsen instrumented impact testing machine of capacity 358 J available at IGCAR, Kalpakkam.

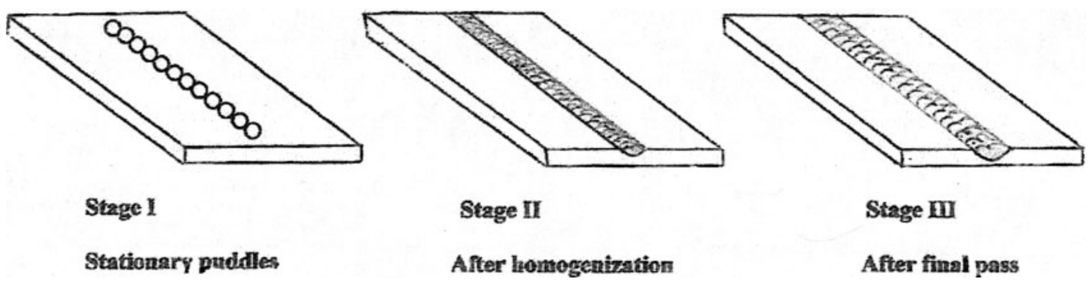


2 Optical micrograph of 304 SS weld showing δ ferrite in weld zone. Etchant: ammonium bifluoride (20 g) + potassium metabisulfite (0·5 g) + distilled water (100 mL)

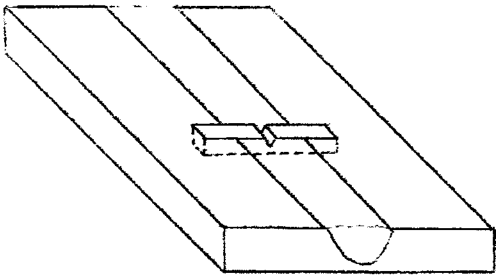
Methods

Modified elemental implant technique

A modified elemental implant technique developed at IGCAR Kalpakkam was adopted to synthesise the specific chemistry of welds. In this technique, the TIG torch was held stationary and arc spot welds (stationary puddles) were made on the centreline of the base metal plate ($200 \times 100 \times 12$ mm). Since the δ ferrite level was more than the accepted level, manual additions of accurately weighed nickel were carried out during welding to bring down the δ ferrite level to FN4–FN6. Homogenisation of elemental additions was later done by giving continuous weld passes at a higher current and higher shielding gas flow rate than that employed in the stationary puddle technique. Two such passes were given to ensure complete homogenisation. A calculated amount of nitrogen (based on Fig. 1[6]) was introduced into the weld metal along with argon by means of a Y connector during the next pass to achieve two more levels of nitrogen, namely 0·08 and 0·11 wt-%, and the final nitrogen contents were confirmed using a Kjeldahl apparatus.. This gives a weld penetration of 6 mm. In order to relieve the welding stresses and to increase the depth of penetration (from 6 mm to 8 mm), homogenised plates were annealed at 1073 K for 1 h. A final weld pass was then made. The weld regions were analysed for their ferrite content using Magne-gage and found to be within FN4–FN6, which was also confirmed by optical microscopic studies (Fig. 2). The various stages of the modified elemental implant technique are shown in Fig. 3



3 Various stages of weld simulation by elemental implant technique



4 Schematic sketch showing orientation of Charpy impact specimen (TS orientation) relative to the weld

Aging treatment

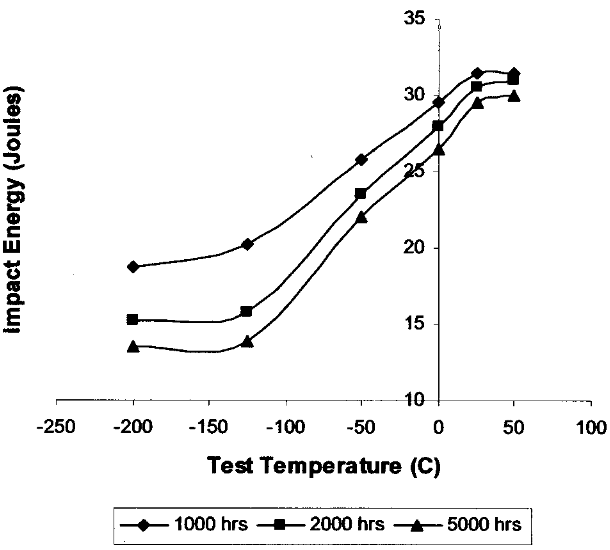
Specimen blanks roughly 6 × 6 × 60 mm suitable for subsize Charpy testpieces were cut from the top layer of the plates in order to get the entire weld cross- section in these specimens. Subsize Charpy impact specimens were chosen for these tests as standard size specimens would require an impact testing machine of higher capacity due to the extensive plastic deformation of austenitic (FCC) material. Further, it is known[7] that subsize samples give results closely matching those of standard size Charpy samples under brittle fracture conditions. Samples were machined so that the weld zone was contained at the centre, occupying the entire cross-section of the specimen.

These rough specimens were then aged in furnaces maintained at different temperatures (623 K, 673 K, and 748 K). Specimens were aged at these temperatures for periods of 1000 h, 2000 h, and 5000 h.

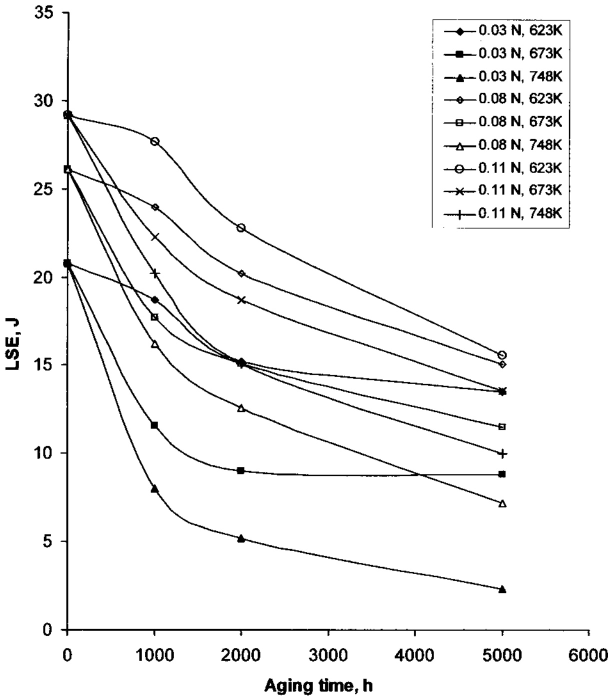
Charpy impact testing

Standard subsize specimens of size 5 × 5 × 55 mm were cut from the 6 × 6 × 60 mm specimens after aging for the required time. V notches (with a notch depth of 1 mm and notch root radius of 0·25 mm) were made at the centre of the weld in TS orientation, as shown in Fig. 4.

Charpy impact tests were carried out on as welded and welded and aged samples at different test temperatures from 77 K to 300 K. The specimens were brought to test temperature, held for 5 min and then subjected to Charpy impact tests. The energy (in joules) absorbed by each specimen before fracture was recorded.



5 Typical Charpy impact curves for 304 SS welds containing 0·03 wt-%N aged at 623 K

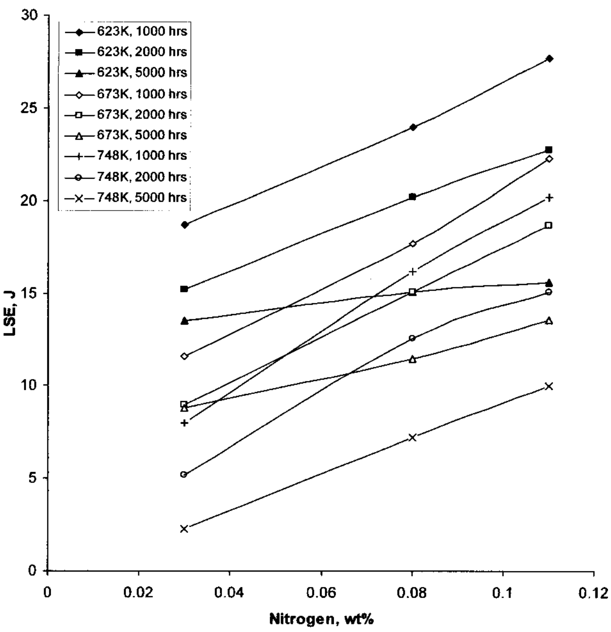


6 Effect of aging on lower shelf energy (LSE) of 304 SS welds containing different levels of nitrogen

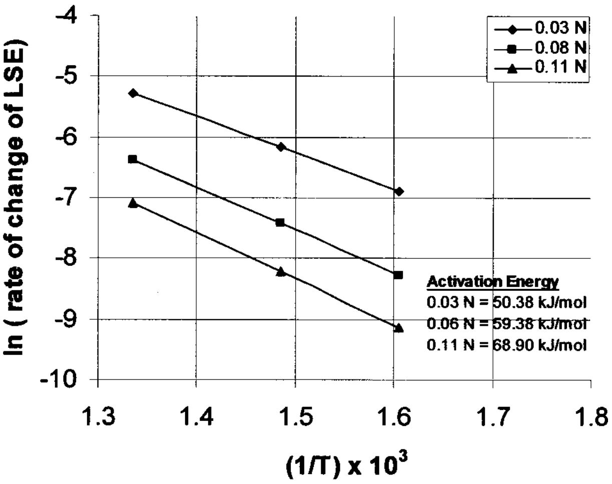
Results

The impact test results were used to generate impact energy versus test temperature plots. Typical plots are shown in Fig. 5. From these plots, the upper shelf energy (USE) and lower shelf energy (LSE) were obtained.

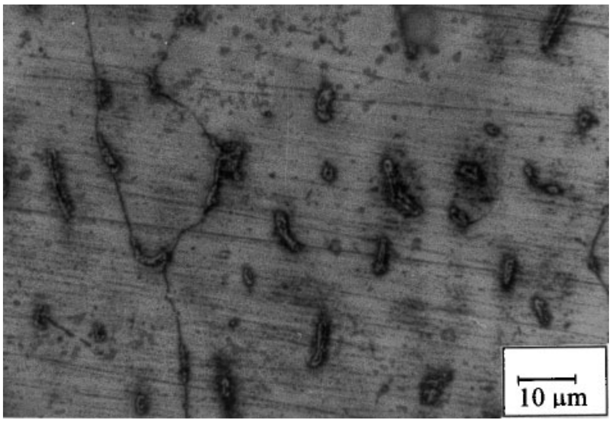
The influence of parameters such as aging temperature, aging time, and nitrogen content on the LSE are shown in Fig. 6 and Fig. 7. Although USE values were



7 Effect of nitrogen on lower shelf energy (LSE) of 304 SS welds aged at various temperatures for different periods of time



8 Arrhenius plot for the calculation of activation energy



9 Optical micrograph of 304 SS weld (0·03 wt-%N) aged at 673 K, 5000 h showing spinodal decomposition of δ ferrite. Etchant: ammonium bifluoride (20 g) + potassium metabisulfite (0·5 m) + distilled water (100 mL)

affected in a similar way, only LSE values are of relevance as the toughness of the material is decided by the level of impact energy shifting to lower values and LSE is always lower than USE.

Discussions

Effect of aging

The lower shelf energies (LSE) were found to decrease with aging time at all aging temperatures (Fig. 6). However, the extent of decrease was greater as aging temperature was increased. δ ferrite in austenitic stainless steel weld metals containing FN4-FN11 decomposes to $\alpha+\alpha'$ at aging temperatures below 763 K, but transforms to σ at temperatures above 813 K. At temperatures within that range, the two transformations occur simultaneously.[8] Upon aging, the ferrite hardness increases and this hardening is accompanied by a noticeable increase in ductile–brittle transition temperature (DBTT) as indicated by Charpy test. Ferrite decomposes spinodally into Fe rich α and Cr rich α' and, in addition, abundant precipitation of Ni and Si rich G phase within ferrite and $M_{23}C_6$ occurs along the austenite/ferrite interface.[9] R(Fe–Cr–Mo–Ni) phase may also precipitate within ferrite.[8] Aging at higher temperatures increases the amount of embrittling phases resulting in lowering of impact energy values. Carbon atoms accelerate the precipitation of G phase in ferrite matrix.[10,11] These effects are similar to the aging behaviour of cast stainless steel.[12] Spinodal decomposition results in embrittlement of welds in so far as the DBTT is raised.

In the present investigation, the apparent activation energy, calculated from the Arrhenius plot (Fig. 8), is found to be on an average 60 kJ mol^{-1} and is in agreement with the reported value of activation energy for spinodal decomposition.[8] This indicates that spinodal decomposition of ferrite is the main cause of embrittlement. Optical micrographs also support this fact as shown in Fig. 9.

Effect of nitrogen on LSE

Increasing nitrogen content increased the lower shelf energies (Fig 7). This improvement in impact energies with increasing nitrogen content is seen at all aging temperatures and aging times.

Embrittlement

For standard impact specimens ($10\times10\times55$ mm) made of ship steels the widely accepted embrittlement criterion is 20 J.[13] For subsize specimens ($5\times5\times55$ mm), as used in the present investigation, where the cross-sectional area is one-quarter of that of standard Charpy specimen, the embrittlement criterion could be taken as one-quarter that of standard specimens, i.e. 5 J since for a perfectly brittle fracture, energy required for fracture is equal to the surface energy of newly created surface only. This is in agreement with the observation that area normalization gives a better fit in the lower shelf region.[7] This is also confirmed by the fact that almost 100% cleavage fracture was observed in those specimens that showed impact energy values less than 5 J.

Based on the above criterion for embrittlement, the worst aging conditions in the present work were identified and are as shown in Table 2.

It is clear from Table 2 that as aging temperature and aging time increase, the resistance of the steels to embrittlement decreases. Thus, the tendency for embrittlement is a strong function of aging parameters aging temperature and aging time. Nitrogen addition is beneficial as the welds with higher nitrogen content show improved resistance to embrittlement.

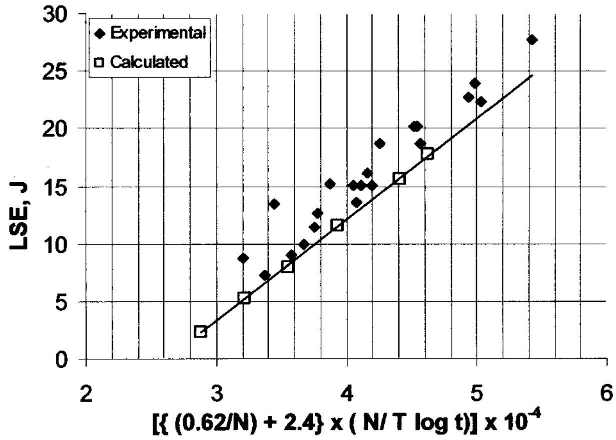
Similar observations have been made in the case of AISI 316 SS material.[14]

Empirical relation

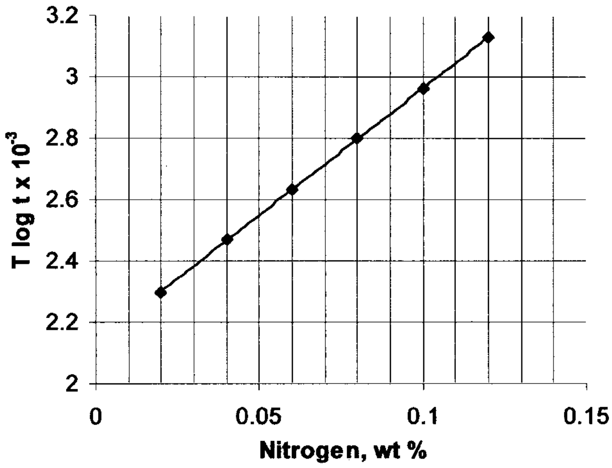
It should be noted from Table 2 that the worst conditions causing embrittlement are seen for the lowest nitrogen levels and as nitrogen content is increased, LSE values for the same aging conditions shift to higher values. Thus, the tendency for embrittlement is a strong function of the parameters aging temperature, aging time, and nitrogen content. Therefore, it is desirable to develop empirical relationships connecting these parameters to LSE. The experimental values were found to

Table 2 Worst aging conditions causing embrittlement as identified in present work

Material	Aging parameters (temp., time)	Impact energy, J
304 SS (0·03 wt-%N)	748 K, 2000 h	5·0



10 Comparison between experimental LSE values and LSE values calculated using the empirical relation



11 Combination of *N*, *T* and *t* to cause embrittlement (i.e. to reduce LSE to 5 J)

be scattered within a narrow band and the lower limit of the band was used to develop an empirical relation for 304 SS as given below:

$$\text{LSE (J)} = [\{(0{\cdot}62/N)+2{\cdot}4\} \times 10^5 \times (N/T \log t)] - 24$$

where T is the aging temperature in kelvin, t is the aging time in hours, and N is nitrogen content in wt-%.

The calculated values from the above equation are in fairly good agreement with the most conservative experimental values, as shown in Fig. 10. However, it should be borne in mind that the above equation has limitations as regards the range of values permitted for each parameter. The equations are valid for nitrogen levels from 0·03 wt-% to the solubility limit in the steels concerned; and aging temperatures between 623 K and 748 K. Below 623 K, aging practically has no significant effect on impact energy due to the extremely slow kinetics of precipitation. Above 748 K, the embrittlement mechanisms are not well established and may be altogether different from those mentioned earlier.

The empirical relation can be used to predict the aging time required to cause embrittlement (to lower the LSE to 5 J) for a given nitrogen content and aging temperature. Using LSE=5 J, a plot of ($T \log t$) versus N was generated, as given in Fig. 11, from which the aging time for embrittlement for a given value of N and T can easily be estimated.

Conclusions

From the investigations carried out, the following conclusions were drawn:

1. Both the upper shelf energy (USE) and lower shelf energy (LSE) are found to decrease with aging time at all temperatures.
2. Nitrogen additions to the welds have a beneficial effect as the resistance to embrittlement increases with increasing nitrogen content.
3. Worst aging conditions for 304 SS were found to be 748 K, 2000 h at the lowest nitrogen level (0·03 wt-%).
4. The empirical relationship developed agrees fairly well with experimental values.
5. The empirical relationship developed can be used to predict the time for embrittlement at a given nitrogen level and aging temperature.

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