COMPETITION BETWEEN SENSITISATION AND ENVIRONMENTALLY INDUCED GRAIN BOUNDARY DAMAGE IN 304 STAINLESS STEEL

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It has been shown that intergranular cracking of 304H stainless steel occurs at several temperatures (-196, 480 and 610°C). This cracking always involves sensitisation (local dechromisation and formation of $M_{23}C_6$ carbides) and a second temperature-dependent factor, which was identified to be martensitic transformation at -196°C, environmental effect at 480°C and mainly intergranular creep process at 610°C. Macroscopic evidence of an intergranular creep process was obtained by slow strain rate tests (10^{-7} s^{-1}, 610°C) performed under oxidising environment or secondary vacuum, which result in intergranular cracking for plastic deformation as low as 2% and lead to fully intergranular fracture. Environmental effect was only observed at 480°C, i.e. just at the lower limit of the sensitisation field in the Time-Temperature-Sensitisation diagram. The importance of sensitisation was confirmed by liquid nitrogen testing, which appears as a simple way to reveal grain boundary weakness.

INTRODUCTION

The renewed interest for studies of the high temperature embrittlement in 304H stainless steels comes from recently observed grain boundary cracking in some bimetallic welds between ferritic steel and austenitic stainless steel [1]. The cracks were found in the first, fully austenitic buttering layer, whose local composition is actually very close to that of 304H stainless steel, mainly because iron and carbon diffuse during welding. One of possible explanation of this cracking directly implicates stress relief heat treatment, which is performed at 610°C under oxidising environment. Sensitisation and strain oxidation would be responsible for the observed embrittlement [2]. Another explanation is based on atmospheric corrosion of the martensite formed in sensitised grain boundaries [3]. This paper takes into account the first hypothesis, with an assumption that 304H stainless steel is representative of the first buttering layer in terms of metallurgical and mechanical behaviour.

The main objectives of this study were (i) to choose the relevant laboratory test to reproduce on 304H stainless steel the intergranular cracking, typical of bimetallic welds and (ii) to analyse the reasons of this intergranular damage in terms of microstructure evolution and environmental effect.

EXPERIMENTAL

The material used in this study is a 304H high carbon stainless steel (Ni-8.5wt%, Cr-18.6, Mn-0.98, Si-0.30, C-0.077, Fe-bal.). Three series of tests were done, either at 610°C or in liquid nitrogen or at 480°C. First, high temperature (T = 610°C) slow strain-rate tensile tests were performed at $d\varepsilon/dt = 1.1 \times 10^{-7}$ s^{-1}, either under vacuum (5×10^{-5} mbar) or in a complex oxidising environment (air + 4%CO_2 + 8%H_2O), on cylindrical (5 mm in

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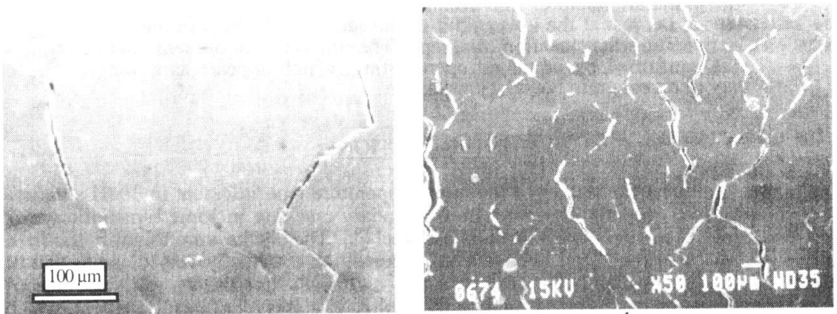
diameter and 22 mm in length), smooth and polished specimens. Secondly, several heat treatments (5min < t < 65h) were performed at T = 610°C and followed by tensile test in liquid nitrogen ($d\varepsilon/dt = 5x10^{-2}\ s^{-1}$, T = -196°C). Finally, another series of specimens was notched and tested up to rupture in order to assess the environmental effect (450°C < T < 610°C, $d\varepsilon/dt = 5.5x10^{-7}\ s^{-1}$, vacuum or air + 4%$CO_2$ + 8%H_2O). Scanning Electron Microscopy was used to investigate fracture surfaces.

RESULTS

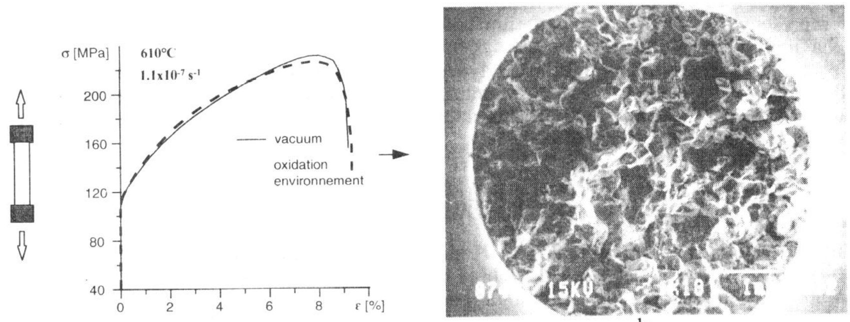
High temperature (610°C) behaviour

Several preliminary tests were conducted on 304H stainless steel at 610°C in oxidising environment under strain-rate controlled conditions, which are representative of deformation that occurs during stress relief heat treatment. It has been shown that, with decreasing strain rate, the number of cracks was increasing, the deformation to rupture was decreasing and the necking was less and less pronounced. Consequently, we have chosen the strain rate of $1.1x10^{-7}\ s^{-1}$, compatible with numerical simulations of deformation rate in bimetallic welds.



a. b.

Fig. 1. Intergranular cracking of 304H stainless steel after 2% (a) and 4 % (b) plastic deformation at 610°C, $1.1x10^{-7}\ s^{-1}$ under air+ 4%CO_2+8%H_2O, (tensile axis is horizontal).



a. b.

Fig. 2. Stress-strain curves obtained on smooth specimens of 304H stainless steel deformed at 610°C, $1.1x10^{-7}\ s^{-1}$ up to fracture, either under air+ 4%CO_2+8%H_2O or under secondary vacuum (a). In each case fracture surface reveals extremely strong intergranular damage after less than 10% plastic deformation (b).

The most striking result of this study is a very strong grain boundary cracking induced by high temperature slow strain rate testing (610°C, 1.1×10^{-7} s^{-1}, air + 4%CO_2 + 8%H_2O, tests stopped after 2 and 4% plastic deformation). The observation of the specimen surface indicates the occurrence of first cracks for plastic deformation as low as 2% (Fig.1a). With increasing plastic deformation (and in the same time, the duration of high temperature exposure) these cracks become longer, wider and oxidised (Fig.1b). The stress-strain curves of two tests conducted up to rupture, the first one under oxidising environment and the second one under secondary vacuum, are characterised by almost the same shape, maximum stress and elongation to rupture (Fig. 2a). In both cases, similar grain boundary cracking on initially smooth lateral surfaces were observed. Furthermore, the fully intergranular fracture after less than 10% plastic deformation, with no evidence of necking, was common for both specimens (Fig. 2b).

Cracking in liquid nitrogen at -196°C

In order to check the depth of the cracks the specimen deformed up to 2% plastic deformation (610°C, 1.1×10^{-7} s^{-1}, air + 4%CO_2 + 8%H_2O) was subsequently broken in liquid nitrogen : thus one would expect to easily distinguish between intergranular cracks opened at 610°C and presumably ductile fracture in liquid nitrogen (304H is characterised by austenitic structure). However, the specimen exhibited fully intergranular fracture (as shown in Fig. 3b), without necking. The maximum depth of the pre-cracks was of the order of 100 µm : in fact, cracks opened at 610°C were easy to locate because strongly oxidised, as opposed to the remaining part of the fracture surface. This result raises at least three important questions : (i) is high temperature deformation necessary for subsequent brittle intergranular fracture in liquid nitrogen?, (ii) what is the kinetics of grain boundary embrittlement? and (iii) what is the phenomenon which causes this brittle fracture in a fcc metal?

In order to answer these questions, several heat treatments were performed at 610°C under vacuum and followed by liquid nitrogen tensile testing. It appears that with increasing heat treatment time, the maximum stress is decreasing (Fig.3a) and the fracture mode abruptly changes from fully ductile with strong necking (heat treatment time t<30 minutes, Fig.3b) to strongly intergranular without necking (t>30 minutes, Fig.3c). Consequently, high temperature deformation is not necessary for subsequent intergranular fracture in liquid nitrogen. A particular shape of stress-strain curves as well as the fact that all specimens became magnetic after test, were very helpful in identifying the phenomenon causing brittle fracture. We notice also that 65 hours heat treated specimen, while tested at room temperature (air, 20°C, 5×10^{-2} s^{-1}), exhibits fully ductile fracture (maximum stress of 600 MPa and 60% plastic deformation). In this last case the specimen was only slightly magnetic.

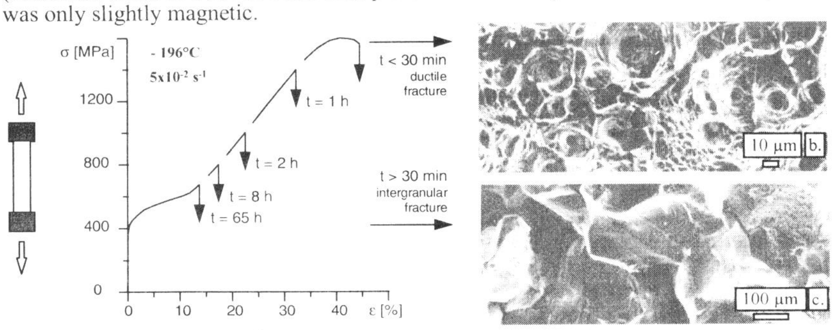


Fig. 3. Stress-strain curves of 304H deformed in liquid nitrogen (-196°C, 5×10^{-2} s^{-1}), as a function of heat treatment duration (up to 65h) at 610°C under vacuum (a). Fracture surface is completely ductile for heat treatments shorter than 30 minutes (b) and clearly intergranular for longer times (c).

Environmental effect at 480°C

A series of slow strain-rate comparative tests, either under oxidising environment or under secondary vacuum, was performed in the 450-610°C temperature range at 5.5×10^{-7} s^{-1} on notched specimens. In general, no significant differences were observed neither in stress-strain curves nor in fracture surfaces (as in Fig.2), which were always the same for a given temperature (intergranular for T > 480°C and ductile for T = 450°C). However, the test performed at 480°C revealed an important decrease of the maximum stress and of the elongation to rupture (Fig.4a), as well as a clear difference in the fracture surfaces. In fact, straining under vacuum resulted in 100% ductile fracture, as opposed to straining under oxidising environment, where numerous intergranular zones were observed at the vicinity of the notch (Fig.4b).

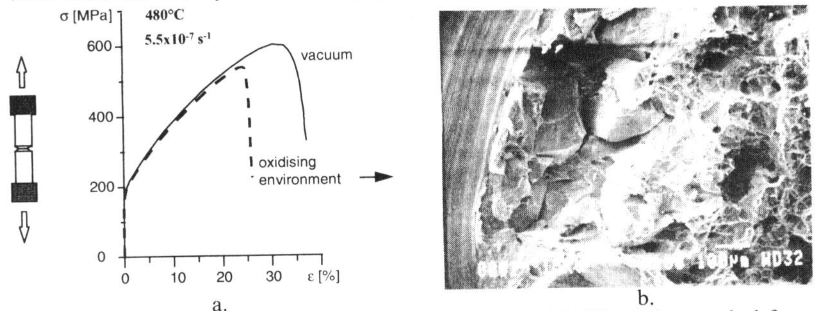


Fig. 4. Stress-strain curves obtained on notched specimens of 304H stainless steel, deformed at 480°C, 5.5×10^{-7} s^{-1} up to fracture, either under air+ 4%CO_2+8%H_2O or under secondary vacuum. Testing under oxidising environment results in significant reduction of elongation to rupture (a) and leads to the formation of several intergranular cracks at the vicinity of the notch (b).

DISCUSSION

Sensitisation

Our results indicate that when specimens were heat treated above 480°C for a sufficiently long time (for example, at least 1h at 610°C), the resulting fracture, at the outcome of either slow strain-rate or liquid nitrogen tests, was fully intergranular. This grain boundaries behaviour can be directly correlated with sensitisation field of 304H steel, as indicated on Time-Temperature-Sensitisation (TTS) diagram (Fig.5, 0.08%C) [4]. Sensitisation implies two phenomena which take place simultanously : $M_{23}C_6$ carbide precipitation and formation of a chromium depletion zone [5]. Both or only one of them contribute to the observed intergranular cracking. However it is important to underline that sensitisation is necessary but not sufficient to cause intergranular fracture, as indicated by room temperature test on the sensitised specimen. Another factor is necessary. Its nature depends on temperature and only the combination of sensitisation and this factor at a given temperature results in intergranular fracture, as shown in three following paragraphs.

Effect of martensitic transformation (-196°C)

In order to explain why liquid nitrogen testing is so effective in revealing grain boundary embrittlement, we have to check the metallurgical behaviour of the 304H steel. In fact, this steel, when plastically deformed at low temperature, exhibits martensitic transformation [6] (responsible for magnetic properties), which strongly raises its tensile strength (up to 1600 MPa at -196°C as compared to 600 MPa at room temperature). This increase of the bulk resistance in liquid nitrogen favours IG fracture in specimens with weakened grain boundaries. Consequently, only the combination of sensitisation and martensitic transformation results in intergranular fracture.

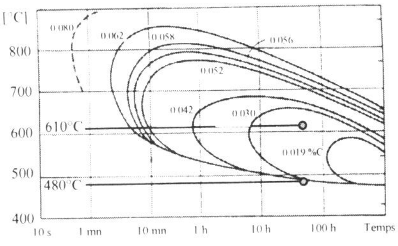


Fig.5. Time-Temperature-Sensitisation curves for 304 stainless steels as a function of carbon content. Our tests were done in the centre (T=610°C) and at the limit (T=480°C) of the sensitisation field.

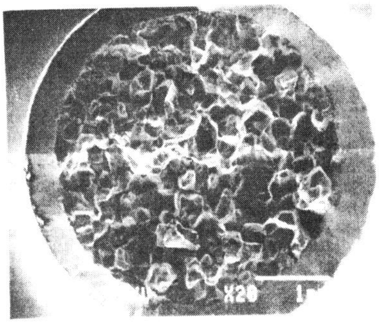


Fig.6. Intergranular fracture surface with ductile external ring. 304H stainless steel deformed in liquid nitrogen (-196°C, 5×10^{-2} s^{-1}), after 2% plastic deformation at 610°C and heat treatment under gaseous hydrogen (1000°C, 20h).

In fact, if one of these factors is absent, the fracture surface becomes ductile, as evidenced by two experiments. First, room temperature testing results in ductile fracture, because the volume fraction of martensite at this temperature is too low (of the order of 20% [6]) to cause a sufficient increase of the bulk stress. Secondly, liquid nitrogen test (-196°C, 5×10^{-2} s^{-1}) on a specimen, which has undergone sensitisation (65h, 610°C) and heat treatment under gaseous hydrogen (20h, 1000°C), also results in ductile fracture. In this second case, the heat treatment is supposed to reduce $M_{23}C_6$ carbides as well as free carbon to a certain depth (0.5 mm in our case), therefore preventing sensitisation in the area which forms a very regular ductile ring on the fracture surface (Fig.6).

Environmental embrittlement (480°C)

The damaging effect of environment has been established out of the sensitisation domain by comparing fracture surfaces after slow strain rate testing at 480°C either in oxidising environment (intergranular areas in the vicinity of a notch) or under secondary vacuum (fully ductile fracture). The degree of vacuum is of prior importance. In fact, the oxygen partial pressure has to be lower than the transition pressure, below which the environment can be considered as inert. This pressure has been found to be of the order of 10^{-3} mbar for a large class of nickel-based superalloys [7], as well as for an austenitic 316L stainless steel [8]. Therefore assuming the same transition pressure for 304H stainless steel, our tests under secondary vacuum (5×10^{-5} mbar) are effectively done in inert environment. The environmentally induced embrittlement observed in this study reinforces recent trend to analyse such fractures in terms of oxidation-deformation interactions [7,9].

Reasons of cracking at 610°C

High temperature cracking is associated with simultaneous action of (i) sensitisation, as indicated by the position of the point (610°C, 65h) in the middle of the sensitisation field (cf. Fig.5) and (ii) intergranular creep process, as indicated by several intergranular cracks on the specimen surface (cf. Fig.1) and fully intergranular fracture surface (cf. Fig.2b). Environmental effect might also be involved in fracture at 610°C, however its contribution seems to be masked in our testing conditions by the predominant role of the two above mentioned factors. Crack propagation test on CT specimens would be more appropriate to analyse the role of oxidising environment [9]. Note also that (i) sensitisation occurs in all specimens deformed under slow strain-rate testing conditions, even those deformed up to only 2% plastic strain at the strain rate of 1.1×10^{-7} s^{-1} (65h at

610°C) and (ii) according to Frost and Ashby [10], intergranular creep process is the deformation mechanism leading to fracture in our experimental conditions.

In general, analysis of intergranular creep process [11] indicates two major contributions : grain boundary sliding in inclined grain boundaries and cavitation in normal (with respect to the tensile axis) grain boundaries. In particular, this analysis was successfully applied to interpret intergranular fracture of 304H stainless steel at higher temperature (760°C) [12].

While there is no doubt about macroscopic parameters (sensitisation and intergranular creep process) which control intergranular fracture at 610°C, the microscopic mechanisms are still obscure. Observations of specimen surface at a finer scale are necessary to provide experimental evidence of grain boundary sliding and cavitation. Furthermore, the precise role of sensitisation has to be addressed. In particular, we try to answer the question whether accelerated cracking in sensitised 304H stainless steel (with respect to 304L) is due (i) to easier grain boundary sliding because of presumably decreased flow stress in the chromium depleted zone or (ii) to faster cavitation on $M_{23}C_6$ intergranular carbides.

CONCLUSIONS

1. Grain boundary cracking observed in bimetallic welds was successfully reproduced on 304H stainless steel, using slow strain-rate testing under controlled environment. This testing method is a relevant way for studying the interactions between internal (sensitisation, intergranular creep) and external (environment) damaging factors.

2. The intergranular cracking of 304H stainless steel at 610°C is attributed to the combination of sensitisation and mainly intergranular creep process.

3. The intergranular embrittlement of 304H stainless steel by oxidising environment was observed at the lower limit of the sensitisation field, i.e. at 480°C.

4. Grain boundary weakening due to the sensitisation of 304H stainless steel can be easily revealed by liquid nitrogen testing where final intergranular fracture is attributed to the combination of sensitisation and deformation induced martensitic transformation.

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