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Journal of Nuclear Materials 283–287 (2000) 1356–1360

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Impurity effects on gas tungsten arc welds in V–Cr–Ti alloys

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Abstract

Plates 6.4 mm thick of V–Cr–Ti alloys, mostly V–4Cr–4Ti, were welded in a glove box argon atmosphere. A hot titanium getter led to excessive hydrogen concentrations. A cold zirconium–aluminum getter was used to reduce both oxygen and hydrogen. It was observed that a major source of hydrogen was dissociation of water vapor by the electric arc of the welding torch. Careful monitoring of atmospheric impurities and successive pumping and backfilling cycles permitted welds of higher quality than previously achieved. Welds were evaluated primarily by the Charpy impact test. A ductile-to-brittle transition temperature (DBTT) of −28°C was achieved in V–4Cr–4Ti. Previous GTA welds in the same material seldom had a DBTT below room temperature. Electron beam welding can achieve a DBTT of below −90°C in the V–4Cr–4Ti alloy, indicating a lower limit to the DBTT by impurity control.

1. Introduction

Before the advantages of vanadium alloys, such as low neutron activation, high thermal conductivity and compatibility with liquid metal coolants, can be exploited in a fusion device, methods for fabricating complex structures must be developed. Welding of vanadium alloys by methods such as gas tungsten arc (GTA) welding has not been reliable due to embrittlement. Electron beam welding can achieve ductile-to-brittle transition temperatures (DBTT) below −90°C, but the large vacuum chambers required for field fabrication of fusion reactors preclude this option. Inertial and conventional friction welding techniques have been used for V–Cr–Ti alloys, especially for the case of dissimilar metal welds, although rigorous testing of the experimental welds has not yet been done [1]. This technique is limited to rather specific sizes and shapes dictated by the rotation of one component. Various degrees of success have been reported using laser welding on thin sheets of vanadium alloys [2]. However, arc welding remains the most likely method to be used for joining large structural components of a fusion reactor.

The success with welding thin sheets cannot be extrapolated to thick plates because thicker plates remain hot for a longer period, thus allowing higher concentrations of impurities to diffuse into the weld zone. The present research focuses on 6.4 mm plates since plates of this thickness are likely to be used in fusion reactor blankets. Moreover, thick plates allow testing by Charpy impact and fracture toughness techniques. Thin sheet is limited mostly to tensile testing but, in the case of specimens cut across a weld, vanadium alloys fracture in the base metal because of interstitial hardening in the weld fusion zone [3].

The present research will attempt to correlate impurities in the welding atmosphere with impurities in the weld and with mechanical properties.

2. Experimental methods

A 6.4 mm plate was machined to form a 75° included angle V-groove butt joint with a 2.4 mm root opening. Filler wire fabricated from the same alloy and heat as the base metal was used to make multi-pass welds of 6–11 passes depending upon the diameter of the filler wire. The arc welds used direct current, electrode negative at a current range of 100–140 A at 12 V. The welds were made manually with a hand-held torch.

A stainless steel vacuum chamber glove box with a volume of 4.7 m^3 and pumped with a 254 mm oil

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diffusion pump was used for all of the GTA welds. After the welding chamber was pumped to a pressure in the 10^{-4} Pa range, it was back filled with high purity argon (99.999%) to a pressure of one atmosphere to permit use of the gloves. Initial welds were made with moisture levels below 40 wt. ppm. When the need for lower levels of water vapor was realized, levels below 1 wt. ppm were used, except in cases of intentional impurity doping. Moisture levels were monitored with a solid state monitor.

Following several welds, it was determined that improvements to the glove box atmosphere were necessary. A purification system was added to the glove box to reduce oxygen contamination. This system consisted of a molecular sieve trap to reduce moisture and a titanium element held at 600–800°C to getter oxygen. A circulation pump circulated argon through the system. This system reduced oxygen to levels below 1 wt. ppm, but it was found that hydrogen levels were increased. This system was abandoned for later welds and replaced by a fixed cold getter system inside the chamber. A zirconium–aluminum getter, SAES No. St 101, was used. [1] This getter system was capable of absorbing both hydrogen and oxygen.

For welds GAGTA2 and GTA18, the atmosphere in the welding chamber was monitored with a residual gas analyzer (RGA). [2] A quadrupole mass spectrometer head was installed in a very small chamber pumped by a turbomolecular pump. The argon welding atmosphere was bled into the GTA chamber through a leak valve in order to maintain a high vacuum in the RGA chamber while sampling the welding atmosphere. This system enabled monitoring of residual gases as well as gases produced during welding. It suffered from the disadvantage that its response was slow due to the very low flow rate through the leak valve and the fact that it was located about 1 m from the chamber, connected by 6.4 mm tubing. Nonetheless, changes in the composition of the atmosphere could be monitored as the weld progressed.

Charpy impact testing was found to be a rapid method of evaluating relative embrittlement of welds. A miniature Charpy specimen, one third of the width and thickness of a standard Charpy specimen, was chosen for the tests based on experience with miniature specimens used for irradiation tests [4]. The specimen was 25.4 mm in length and 3.33 mm on a side with a blunt notch making a 30° included angle machined to a depth of 0.66 mm.

The alloy studied in the most recent welds was V–4Cr–4Ti (Wah Chang heat 832 665). A few welds were made with the same alloy of Wah Chang heat 823 864, which was demonstrated to have impact properties similar to the previous heat [5]. However, the filler metal was from heat 832 665 so that the fusion zone was of the same material as the other welds. Early studies were made on V–5Cr–5Ti (Wah Chang heat 832 394), which also had similar properties following a heat treatment of 950°C for 2 h [6]. Because all three heats had similar properties and the notch in the Charpy specimens was in the center of the fusion zone of the welds, the results of welds from all three heats and both alloys have been compared directly. In addition, since all of the Charpy specimens were machined such that the crack propagated entirely within weld metal, the orientation with respect to the rolling direction of the plate was essentially irrelevant.

3. Results

3.1. Oxygen effects

Oxygen is the most common interstitial embrittling agent in vanadium alloys. It is both rapidly-diffusing and ubiquitous. It was observed in Nb–1Zr that oxygen in solution is far more damaging than oxygen in a precipitate [7]. Certainly oxygen is a stronger hardening agent in solution than in a precipitate. This was demonstrated in V–Cr–Ti alloys with respect to embrittlement [8]. Experimental difficulty in separately measuring oxygen in solution and oxygen in precipitates clouds the interpretation of the results. The oxygen concentrations given in Table 1 are total oxygen concentrations measured by vacuum fusion analysis. The oxygen that is damaging to weld properties is that in solution, which could be a small fraction of the total oxygen. For this reason, variation in the total oxygen measurements can sometimes overshadow the trends caused by what are small increases in total oxygen but large increases in the fraction of oxygen in solid solution. Therefore, total oxygen should be used only as a guide; a more reliable measure of contamination appears to be the concentrations of contaminants in the welding atmosphere.

In the present study, the effect of oxygen on welds was demonstrated by intentionally introducing impurities into the welding atmosphere for welds GTA 14 and 15, with GTA 13 serving as a control. Although moisture increased as well as oxygen, a correlation between atmospheric purity and DBTT was suggested, as seen in Table 1. Hydrogen increased slightly, but this was a lesser effect at the levels observed, as will be discussed in Section 3.2. The rapid cooling associated with the welding process quenched impurities in solid solution. A precipitation heat treatment of 950°C for 2 h caused a reduction of the DBTT by about 140°C in the most impure weld by removing oxygen from solution [6].

[1] Manfactured by SAES Getters, Milan, Italy.

[2] Model 100 C, manufactured by UTI, Sunnyvale, CA, USA.

Table 1
Impurity concentrations (wt. ppm) and DBTT (°C)

Weld	O[a]	H_2O[b]	N[c]	H[c]	DBTT
Base metal (832665)	330		100	1–2	<−150
GTA 13	4/374	23	104		57
GTA 13[d]					60
GTA 14	14/352	84	110	21	82
GTA 14[d]					80
GTA 15	27/412	260	146	15	228
GTA 15[d]					86
GTA 16	0.8/370	25	107	63	85
GTA 16[d]					38
GTA 17	<1/347	<1	99	99	20
GTA 17 (400°C/1 h)				1.9	∼0
GAGTA2	1.2/344	5.0		4.5	−27[e]
GTA 18	0.3/333	2.0		2.3	−20

[a] Welding atmosphere (b)/fusion zone concentration(c).
[b] Monitored by electrochemical cells.
[c] Measured by inert gas fusion analysis.
[d] Post weld hear treatment 950°C/2 h.
[e] Few points forced a poor curve fit.

However, the same treatment produced an insignificant improvement in the highest purity weld. This might be expected since little oxygen would have been introduced into solution in such a pure atmosphere. The precipitates resulting from this heat treatment have been identified as $Ti_{16}(O_3N_3C_2)$ [6]. Earlier analyses have identified precipitates of slightly different composition, but all observations are consistent with the conclusion that less pure atmospheres result in a higher volume fraction of precipitates after a post-weld heat treatment (PWHT). Mechanical properties improve upon precipitation of interstitials following a PWHT. It is an important observation that, in the case of welds sufficiently low in interstitial impurities, a post-weld precipitation heat treatment is not necessary.

It has been observed that fracture in oxygen embrittled material is entirely by cleavage at low temperatures on the lower shelf of the Charpy impact curves. In the case of especially oxygen-rich alloys, precipitates are present on grain boundaries as well as in the matrix, and there is some evidence of intergranular fracture accompanying the predominant cleavage. Further details of oxygen effects have been reported previously [6].

3.2. Hydrogen effects

The vacuum heat treatment used in the fabrication of the vanadium plate resulted in hydrogen concentrations below 2 wt. ppm. As can be seen from Table 1, hydrogen concentrations increased following welding. When the oxygen purification system was used, oxygen concentrations in the atmosphere were significantly reduced, but the resulting hydrogen concentrations in the fusion zones increased: 63 wt. ppm (3000 at. ppm) in weld GTA 16 and 99 wt. ppm (5000 at. ppm) in weld GTA 17. This was initially attributed to reduction of water by the hot titanium getter. Use of the getter purification system was discontinued and a cold getter, as previously described, was used, beginning with weld GTA 18. Weld GAGTA2 was made without the benefit of the getter. However, an RGA was installed on the welding chamber, and the atmosphere was very carefully controlled and monitored, purging when necessary. During welding of GAGTA2, it was observed that the hydrogen peak, which was a factor of 20 below the argon peak prior to making the weld, increased as soon as the arc was struck and reached a level about half of the argon peak. Part of this increase was due to the poor pumping efficiency of hydrogen with respect to heavier gases by both the turbomolecular pump on the RGA chamber and the diffusion pump on the welding chamber. In any case, it demonstrated that the previous conclusion that the titanium getter was the primary source of the hydrogen contamination of the weld was incorrect. In fact, the arc itself generates hydrogen by dissociation of water. Because of this discovery, an ultraviolet lamp was subsequently used to desorb water from the chamber walls. The benefit of this UV treatment is questionable, but will be investigated further.

As can be seen from Table 1, welds GAGTA2 and GTA 18 have probably the best combination of atmospheric oxygen and moisture coupled with the lowest hydrogen concentrations in the weld metal and also have the lowest DBTT. Although the table shows GAGTA2 to have a slightly lower DBTT, scatter in the data results in a poor fit to the model used to determine DBTT, Fig. 1. Weld GTA 18 appears to have better properties as seen from the curve, which also appears in Fig. 1.

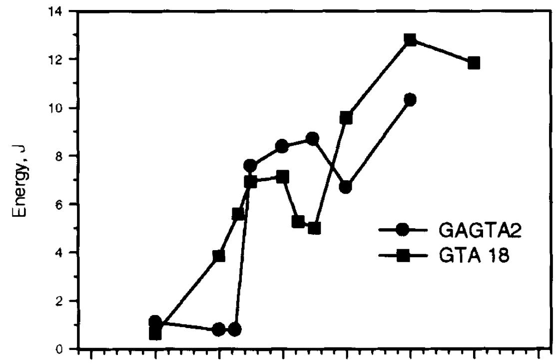

Fig. 1. Charpy energy data showing the high-temperature minima for two GTA welds in V–4Cr–4Ti.

4. Discussion

The effects of atmospheric contaminants can be seen from Table 1, especially from the impurity test series, GTA 13–15. The reported oxygen concentrations in the weld metal are from inert gas fusion analysis, where the sample is melted; thus, oxygen both in solution and in precipitates is measured. Without additional tests, it is not possible to tell how much of the total oxygen reported in Table 1 is in solution where it embrittles the lattice. For this reason, there is not a perfect monotonic relationship between total oxygen concentration and DBTT. However, newly added oxygen, as indicated by the oxygen concentration in the atmosphere, does appear to correlate with DBTT.

For welds where hydrogen is present in high concentrations, the relationship is less clear. In the case of welds intentionally doped with oxygen, a precipitation heat treatment of 950°C for two hours restores most of the ductility loss. Apparently, the concentration of oxygen in solution was reduced. In the case of hydrogen, an outgassing heat treatment of 400°C for one hour removes hydrogen, as demonstrated by GTA 17 in Table 1. A reduction in the concentration of hydrogen reduces the DBTT by mitigating both solution hardening and hydride embrittlement [9,10]. The Charpy energy curves for welds GTA 16 and 17 are shown in Fig. 2 both before and after the outgassing treatment. In both cases, the DBTT is reduced, if the precipitous drop at the lower temperature defines the DBTT, but the outgassed material exhibits large dips in Charpy energy to nearly lower shelf values at 50°C and 100°C. If these were the only examples of such behavior, they would be dismissed as resulting from pre-existing defects. However, such behavior has been observed in V–4Cr–4Ti following heat treatments at 400°C, 750°C, 850°C, and 950°C. In all cases, the fracture surfaces at the ductility minima exhibit almost entirely cleavage fracture whereas fracture surfaces at the ductility maxima exhibit mostly ductile rupture. Examination of the Charpy curves for the highest purity welds, GTA 18 and GAGTA2 (Fig. 1), also exhibit well-defined minima at 22°C and 50°C, respectively. These last two curves are for material that has not been outgassed, but the hydrogen concentrations are nearly as low as those of the outgassed specimens. Clearly, this is a real phenomenon.

The dips in the curves are above the hydride solvus for the concentrations of hydrogen experienced [11]. In addition, the embrittlement phenomenon is more prevalent in the absence of hydrogen. A mechanism of deformation that can take place at the high deformation rates of a Charpy test is twinning, which has been observed in vanadium at low temperatures or high strain rates [12–14]. Indeed, twinning is enhanced by high strain rates, low interstitial concentrations and large grain size, all of which are present [12,15]. Fig. 3 shows a transmission electron micrograph of weld GTA 17 after hydrogen removal. The large plates, on {1 1 2} habit planes, have been identified as twins by electron diffraction. Fewer twins were observed in the weld material prior to the hydrogen outgassing treatment.

The existence of twins alone does not explain the observed behavior of the Charpy energy. Twinning is an additional mechanism of plastic deformation. It can permit deformation in cases where slip cannot occur, thus preventing fracture, or it can nucleate cleavage fracture, for example at the intersection of twins [16–18]. The mechanism suggested can be better understood from Fig. 4. Here, the flow stresses for shear and twinning are plotted schematically with the stresses for initiation of cleavage failure by shear and twinning. Which mechanism has a lower energy for the initiation of a cleavage crack depends on many factors such as grain size, stacking fault energy, impurity concentration and

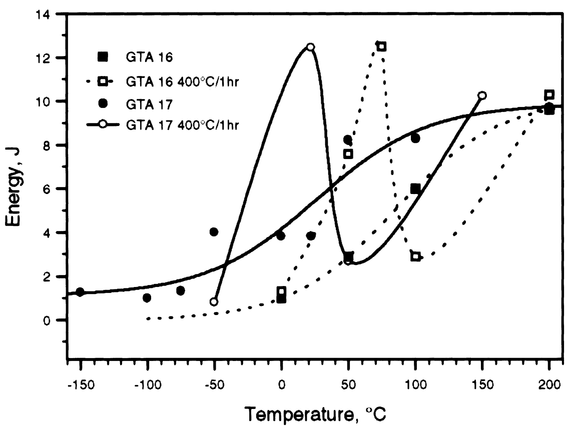

Fig. 2. Charpy energy plot for two GTA welds before and after outgassing at 400°C/1 h.

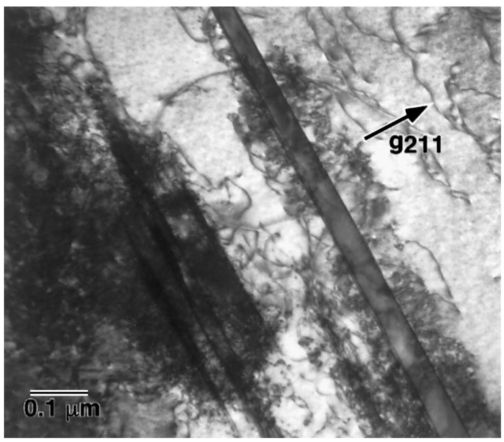

Fig. 3. Transmission electron micrograph showing twins in weld GTA 17 following removal of hydrogen.

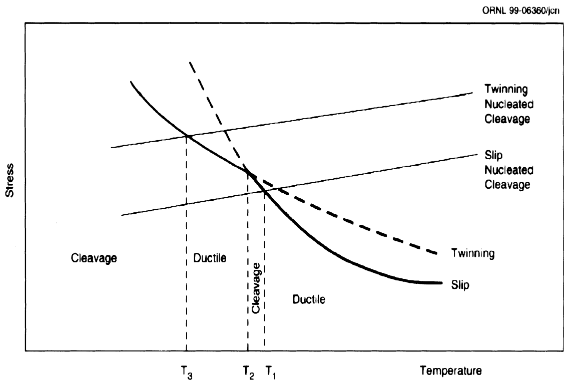

Fig. 4. Schematic of temperature dependence of plastic flow and cleavage showing mechanism by which twinning introduces a second region of ductility.

strain rate, but the temperature dependence is believed to be similar [19]. It will be assumed that the stress for initiation of a cleavage crack by twinning is higher than that for slip. This is a possible situation and a necessary condition to explain the observed behavior. As temperature is reduced, ductile failure by slip gives way to cleavage failure at T_1. As temperature is reduced further, the deformation mechanism changes from slip to twinning as it becomes energetically favorable at temperature T_2. Since the mechanism of deformation has changed, the cleavage initiation energy is now given by a higher curve; thus ductile shear failure returns until temperature T_3 is reached, below which only cleavage results. The region between T_1 and T_2 represents the observed dip in the Charpy curves.

5. Conclusions

1. Gas tungsten arc welds can be made in 6.4 mm plates of V–4Cr–4Ti with a DBTT of −20°C to −30°C.
2. Both oxygen and hydrogen are important impurities that must be controlled in order to weld vanadium alloys.
3. Hydrogen results mostly from decomposition of water vapor by the welding arc, even at low concentrations.
4. Twinning becomes an important deformation mechanism in high-purity vanadium alloys, leading to two regions of embrittlement. In the absence of twinning, the DBTT would be expected to occur at the higher embrittlement temperature.
5. Other factors such as grain size must also be controlled in order to reduce the DBTT still further. The narrowly focused electron beam used in electron beam welding results in a grain size, smaller by a factor of two, which, along with the high vacuum atmosphere leads to a DBTT of the order of −100°C. This is the goal of continued research on arc welding.

Acknowledgements

This research was sponsored by the Office of Fusion Energy Science, US Department of Energy, under contract DE-AC05-96OR22464 with the Lockheed Martin Energy Research Corporation. The authors extend their appreciation to R.L. Klueh and J. Bentley for many helpful discussions and assistance. The authors are also grateful to R.W. Reed, J.D. McNabb, E.T. Manneschmidt and R.L. Swain for their experimental work.

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