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CRADA Final Report
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FEASIBILITY OF CORRELATING V-Cr-Ti ALLOY WELD STRENGTH WITH WELD CHEMISTRY

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Prepared by the
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This work was supported by a CRADA with Charles Evans and Associates, Redwood City, CA, sponsored by the Small Business Technology Transfer Program, Office of Energy Research, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation

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ABSTRACT

The mechanical properties of refractory metals such as vanadium are determined to a large extent by the interstitial impurities in the alloy. In the case of welding, interstitial impurities are introduced in the welding process from the atmosphere and by dissolution of existing precipitates in the alloy itself. Because of the necessity of having an ultra-pure atmosphere, a vacuum chamber or a glove box is necessary. In the V-Cr-Ti system, the titanium serves as a getter to control the concentration of oxygen and nitrogen in solid solution in the alloy.

In this project the secondary ion mass spectrometry (SIMS) technique was used to detect, measure, and map the spacial distribution of impurity elements in welds in the alloy V-4Cr-4Ti. An attempt was then made to correlate the concentrations and distributions of the impurities with mechanical properties of the welds. Mechanical integrity of the welds was determined by Charpy V-notch testing. Welds were prepared by the gas-tungsten-arc (GTA) method. Charpy testing established a correlation between weld impurity concentration and the ductile to brittle transition temperature (DBTT). Higher concentrations of oxygen resulted in a higher DBTT. An exception was noted in the case of a low-oxygen weld which had a high hydrogen concentration resulting in a brittle weld. The concentrations and distributions of the impurities determined by SIMS could not be correlated with the mechanical properties of the welds.

STATEMENT OF OBJECTIVES

The research project had the following objectives:

1. To determine the concentration and distribution of H, C, N, O, P, S, Ti, Cr, and V in representative vanadium alloy welds using SIMS and SIMS ion imaging techniques.

2. Where appropriate, attempt to determine the distribution of precipitates in selected welds using SEM, TEM, internal friction, or scanning tunneling microscopy.

3. Correlate physical test data for selected samples with chemical composition data. Physical tests will include hardness and Charpy tests.

BENEFITS TO THE DOE OFFICE OF FUSION ENERGY SCIENCES

This research supports the DOE OFES effort to develop fusion reactor first wall and blanket structural materials. Vanadium alloys are being considered for first wall and blanket structures for several reasons. One is that they are not strongly activated by neutron irradiation, and the nuclides that are formed by transmutation do not have excessively long half lives. Another advantage is that vanadium alloys have higher thermal conductivity and lower thermal expansion, at operating temperatures, than candidate ferritic alloys, which leads to their ability to carry higher heat loads. Despite these advantages, there are many difficulties with their use, mostly involving contamination by impurities, especially hydrogen and oxygen. Since even a near-term fusion device would have several kilometers of welds, the integrity of vanadium welds could be life-limiting for the device.

In the present research, the correlations developed between impact properties and impurity concentrations provided valuable direction in developing welding techniques for V-Cr-Ti alloys. The necessity for control of hydrogen in the welding atmosphere was discovered in preparing a series of welds with differing concentrations of oxygen. In mapping impurities following welding, it was anticipated to establish the background information needed for making a portable instrument to determine the integrity of a weld in the field. However, this correlation could not be established.

TECHNICAL DISCUSSION OF WORK PERFORMED

Preparation of Weld Specimens

A series of welds was made using glove box atmospheres of argon with various levels of oxygen and moisture. A plate of V-4Cr-4Ti, manufactured by Wah Chang of Albany, OR, as Heat 832665 was used for the study. After a gas-tungsten-arc weld was made joining two narrow plates, a portion of the weld was machined into Charpy impact specimens, and another sample was polished for SIMS investigation.

The 6.4 mm plate was machined with a 75° included angle V-groove butt joint positioned with a 2.4 mm root opening. Filler wire made from the same alloy and heat as the base metal was used to make multi-pass welds using direct current, electrode negative, at a current range of 100 to 140 amperes at 12 volts.

All welds were made in an argon atmosphere in a glove box which was a 4.7 m^3 stainless steel chamber that could be evacuated to 10^{-4} Pa with a diffusion pump. It was back filled with high purity argon to one atmosphere to enable the use of the gloves.

After several welds were evaluated, it was determined that improvements in the glove box atmosphere were required. To reduce the contamination by oxygen, a purification system was added to the glove box. The system consisted of a titanium element held at 600-800°C, a molecular sieve trap to reduce moisture, and a circulation pump. The addition of this system permitted oxygen levels below 1 ppm in the atmosphere in order to achieve a range of levels suitable for the SIMS investigation.

Since fracture and embrittlement appear to be the most important properties to investigate in welds in vanadium alloys, the Charpy specimen was chosen for the present study. A miniature Charpy impact specimen with a length of 25.4 mm and 3.33 mm on a side was used. A blunt notch making a 30° included angle was machined to a depth of 0.66 mm.

The samples for SIMS investigation were ground and polished with standard metallographic techniques, with the exception that no water or aqueous solutions were used. This was done to assure that no hydrogen was introduced in the polishing process. When a fresh surface of vanadium is exposed to water, hydrogen is introduced in concentrations of tens of wt. ppm, depending upon conditions. Since grinding and polishing removes the ever-present oxide coating, water cannot be allowed to contact the specimen.

Evaluation of Mechanical Properties

To study the effects of impurities, a series of welds was made with varying levels of impurities. Using the titanium gettering system described previously, an especially pure welding atmosphere was achieved with an oxygen level of 4 wt. ppm and a moisture level of 23 wt. ppm. A high-purity weld, made using the gettering system, and two additional lower-purity welds, made by deliberately raising the impurity levels in the glove box atmosphere were produced. The welds were designated GTA 13 through GTA 15, and the atmospheric impurity levels are given in Table 1.

Table 1. Impurity Concentrations and DBTT for GTA Welds

		Welding Atmosphere		Fusion Zone Concentration			
Weld	PWHT	Oxygen Wt. Ppm	Moisture Wt. Ppm	Oxygen Wt. Ppm	Nitrogen Wt. Ppm	Hydrogen Wt. Ppm	DBTT °C
GTA 13	None	4	23	374	104		57
GTA 13	950°C/2h						60
GTA 14	None	14	84	352	110	21	82
GTA 14	950°C/2h						80
GTA 15	None	27	260	412	146	15	228
GTA 15	950°C/2h						86
GTA 16	None	0.8	25	370	107	63	85
GTA 16	950°C/2h						38

The concentrations of interstitial impurities in the welds are also shown in Table 1, and a correlation, although not perfect, is demonstrated between the impurity levels in the atmosphere and the oxygen and nitrogen levels in the metal as determined by inert gas fusion analysis. The influence of impurity levels on the DBTT is also evident with a clear monotonic relationship between atmospheric impurity levels and DBTT. Although embrittlement is sensitive to the level of atmospheric impurities, the internal levels of O and N do not change very much. It is believed that most of the O and N from the atmosphere forms a solid solution in the metal. Since much of the pre-existing O and N is in precipitates, the total concentrations do not change by a large amount, but the levels in solution change by a more significant amount, and it is impurities in solution that cause embrittlement.

It has been established from earlier experiments that a post-weld heat treatment (PWHT) improves the Charpy impact properties significantly, reducing the DBTT by as much as 200°C.[1] A heat treatment of 950°C for 2 hours permits oxygen to form precipitates with the titanium in the alloy, thus reducing the concentration of oxygen in solid solution where it is a strengthening and embrittling agent. The welds were tested by Charpy impact both prior to and following such a heat treatment.

Figures 1 and 2 compare Charpy curves for the three welds of the impurity series before and after the PWHT. The effect of the PWHT on the impure weld is rather dramatic with a shift in DBTT of nearly 200°C. The two welds with lower impurity levels, however, show little if any shift in DBTT. It can be concluded from this observation that, if the atmospheric oxygen level is low initially, the precipitation PWHT is not necessary.

The impurity series of welds, GTA 13-15, was extended using a very high purity atmosphere where the oxygen level was below 1 wt. ppm. This weld, GTA 16, however, exhibited a DBTT about the same as that of the intermediate purity weld, Fig. 3. Further analysis revealed the presence of 63 wt. ppm (3200 at. ppm) hydrogen. An out-gassing treatment of 400°C/1hr to remove hydrogen restored most of the original ductility. The attempts to reduce the level of oxygen in the glove box led to an increase in hydrogen. Although titanium is an excellent getter for oxygen in the range of 600-800°C, no hydride phase exists at reasonably attainable concentrations of hydrogen at these temperatures.[2] The result is reduction of water by the hot Ti and release of hydrogen into the welding glove box. From this observation, the need for a hydrogen getter in addition to the heated Ti was identified.

Hydrogen alone is capable of causing severe embrittlement in vanadium and its alloys. However, at the temperatures of the testing, 63 wt. ppm would not be expected to form embrittling hydride. In the presence of high concentrations of oxygen, V-Cr-Ti alloys have demonstrated a synergism between oxygen and hydrogen in causing embrittlement.[3] It is suggested that this results from strengthening the lattice and thus increasing the shift in the hydride solvus temperature due to stress. It is also possible that water is being formed at grain boundaries, leading to stress-rising intergranular crack tips that initiate cleavage fracture. A specimen was examined in a cold stage with transmission electron microscopy, but a diffraction pattern from ice could not be observed.[4] This is, however, a difficult experiment so that the possibility of water vapor embrittlement could not be ruled out.

SIMS Observations

Secondary ion mass spectrometry was done by Charles Evans and Associates. SIMS analyses were performed on a CAMECA IMS-4f Ion Microanalyzer which is a double focusing, stigmatic imaging mass spectrometer equipped with O_2^+ and Cs^+ primary ion sources. Negative secondary ion detection was utilized because of its higher detection sensitivity for such electronegative elements as C, O, F, P, S, and Cl. In addition, H, V, and N were analyzed in the negative ion mode. Both SIMS depth profiling and SIMS image depth profiling were employed in this study. Secondary ion images map the intensity and lateral distribution of various mass selected ions and are formed either in ion microprobe or ion microscope imaging configurations. Ion microprobe techniques utilizing a tightly focused primary beam which is rastered about the sample surface were employed for all results of this study.

However, the concentrations observed in the fusion zones of the welds could not be reliably or quantitatively correlated with the embrittlement observed in the Charpy tests. The ability to discern differences of impurity concentrations and to correlate the distributions and concentrations with mechanical properties is a primary goal of this research. However, the SIMS technique did not detect significant concentration differences for those trace elements suspected of reducing weld integrity. In fact, trace element concentrations of weld and base metal regions were found to be comparable, within the SIMS microanalysis image and depth resolution of 2-4 μm and 5 nm, respectively.

This observation leads to the following general conclusions:

1. Within the 5 μm depths investigated, there is no observed correlation between trace element concentration or distribution and weld integrity in GTA welds of V-4Cr-4Ti.

2. If weld integrity is dependent on the concentration of select trace elements, this dependence is operative at lateral or depth scales below 1 μm.

Based on the results of bulk chemical analysis and Charpy impact tests, there is confidence that there is a strong correlation between impurity behavior and mechanical properties of welds; however, to the surprise of the investigators, state-of-the-art secondary ion mass spectrometry/ion imaging does not have sufficient lateral or depth resolution to detect this correlation. In fact no related ion mass analysis techniques are likely to achieve the necessary resolution and sensitivity. As a consequence, it was decided to terminate the SIMS portion of the research.

INVENTIONS

There are no inventions specifically associated with this CRADA.

COMMERCIALIZATION POSSIBILITIES

The welding of vanadium alloys remains in the laboratory stage. Not only is the technique of mapping impurities not yet developed, welding of this class of alloys itself is not ready for commercialization.

PLANS FOR FUTURE COLLABORATION

Although the SIMS technique did not prove to be valuable in discerning between good and bad welds, impurities remain the major cause of embrittlement in vanadium alloys.

Analytical techniques to determine which impurities are present, their concentration, and their location might still be explored. If vanadium alloys are to be used in large, complex structures, non-destructive evaluation techniques must be developed. Further collaboration might concentrate on another technique for impurity evaluation.

CONCLUSIONS

1. GTA welds were made in 6.4 mm plates of V-Cr-Ti alloys with a DBTT of 50 C. This DBTT could be attained either by making a high purity weld or by using a post-weld heat treatment.

2. A getter system to reduce the atmospheric concentration of oxygen resulted in higher concentrations of hydrogen. An additional getter specifically for hydrogen must be added to the welding glove box.

3. Although SIMS is a very useful tool for determining the distribution of impurity elements, in this case, it could not be used to obtain concentrations that could be correlated with mechanical properties of the welds.

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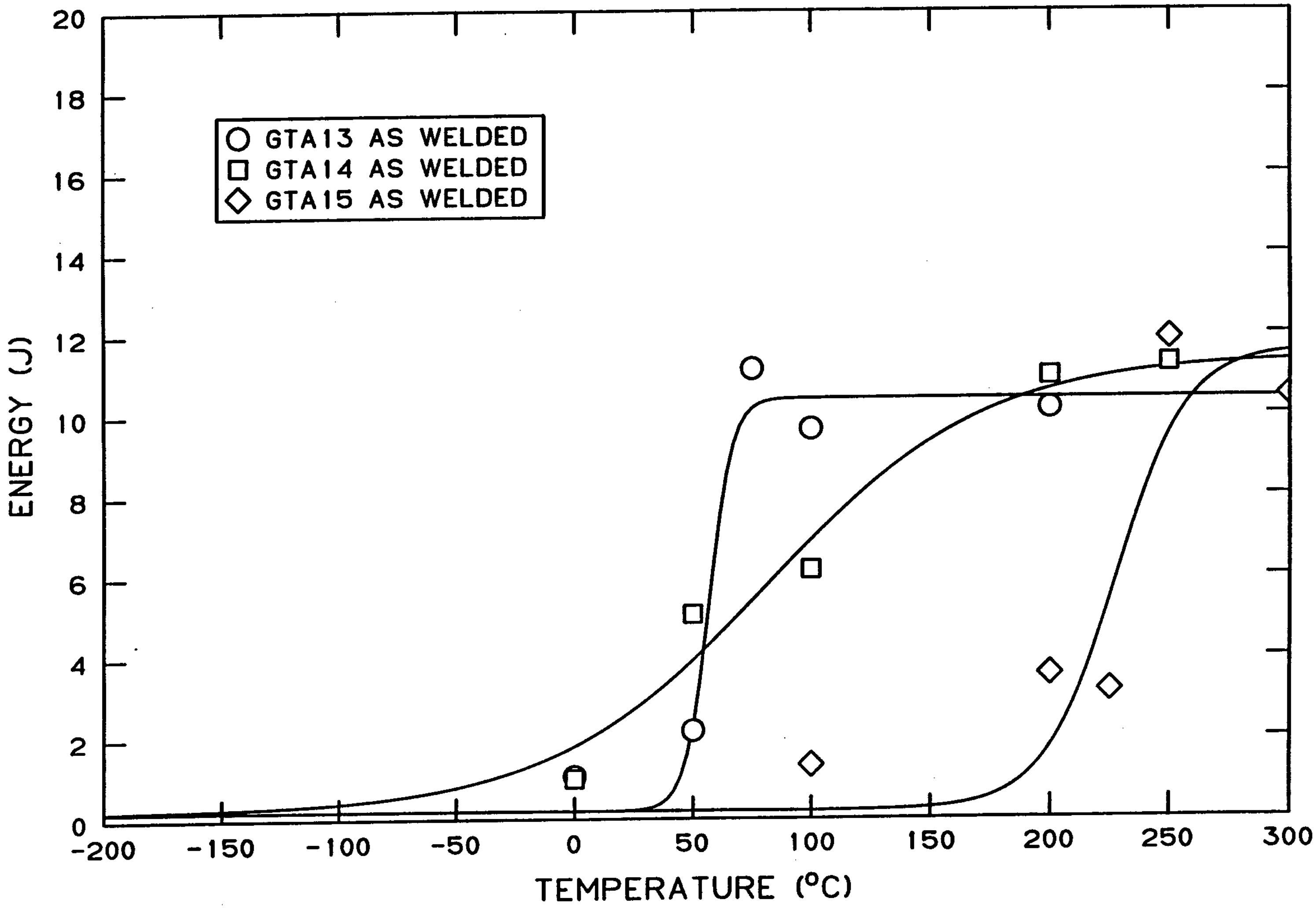

Fig. 1. Absorbed energy as a function of test temperature for Charpy impact tests of GTA welds in V-4Cr-4Ti with differing levels of impurities.

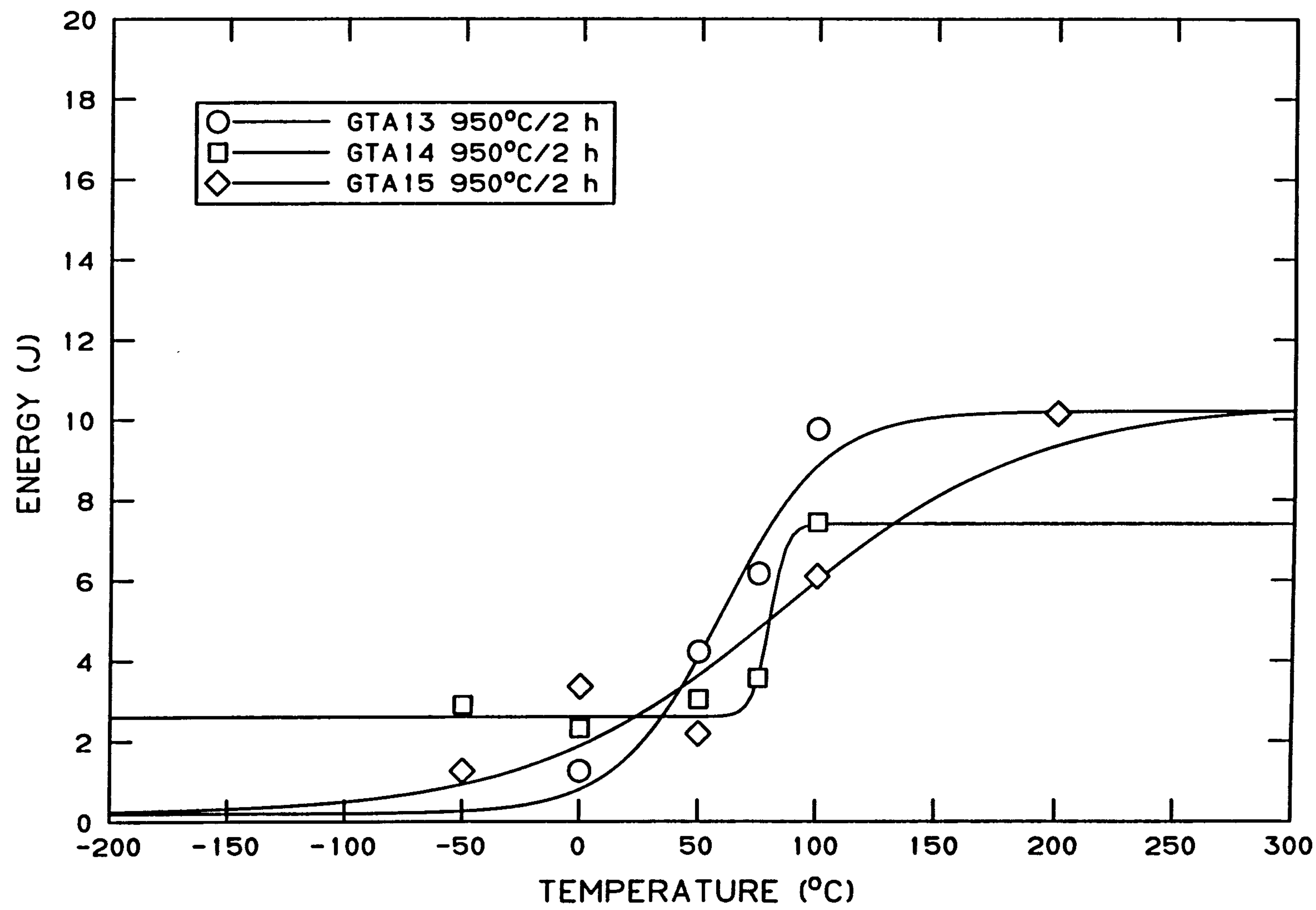

Fig. 2. Absorbed energy as a function of test temperature for Charpy impact tests of GTA welds in V-4Cr-4Ti with differing levels of impurities following a post-weld heat treatment of 950°C for 2 hours.

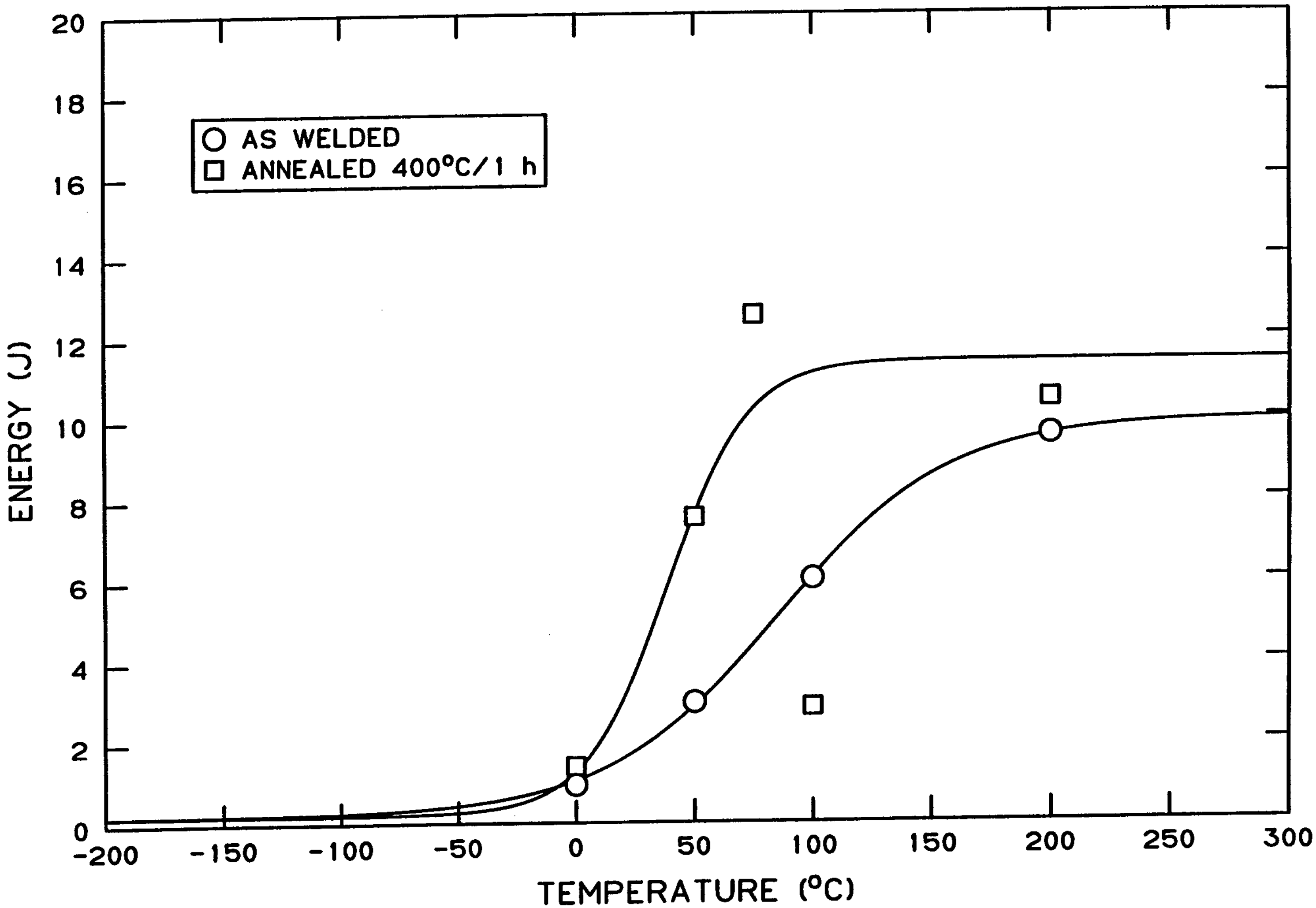

Fig. 3. Absorbed energy as a function of test temperature for Charpy impact tests of a GTA weld in V-Cr-4Ti with low oxygen but high hydrogen concentrations. The hydrogen was removed by an out-gassing treatment of 400°C for 1 hour producing the results by the square symbols.

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Report Number (14) ORNL/M--6554

Publ. Date (11) 199806

Sponsor Code (18) DOE/ER , XF

UC Category (19) UC-400 , DOE/ER

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