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FINAL REPORT

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HYDROGEN ATTACK OF STEEL

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The hydrogen attack of pressure vessel steel is due to the nucleation and growth of small (submicron to micron) bubbles of methane. Thus understanding the kinetics of hydrogen attack requires a knowledge of the number of bubbles that nucleate, the methane pressure maintained within the bubbles, and the growth limiting processes for the bubbles. The kinetics of the hydrogen attack of carbon steels is reasonably well understood. The bubbles nucleate on the grain boundaries to form a close-packed array of a few microns spacing. And, the methane pressure is that in equilibrium with the ambient hydrogen pressure and cementite. There are kinetic models available to describe the growth of the grain boundary bubbles, which draw heavily on those developed for void growth in specimens undergoing creep.

A sensitive dilatometer which we have developed allows the measurement of the growth rate as a function of temperature and hydrogen pressure. Using kinetic models these data can be extrapolated to predict the behavior of the steel at longer times and somewhat lower temperatures.

When this project was started approximately two years ago we wished to see if comparable progress could be made to establish the kinetics of hydrogen attack in commercial quenched and tempered (Q&T) 2-1/4Cr-1Mo steel, and to compare the performance of the weld-metal with that of the base-metal. At that time there were no published reports on the relative rates of hydrogen attack of weld-metal, and very little on the kinetics of the attack of Q&T 2-1/4Cr-1Mo steel. The questions we wished to answer were:

Can the dilatometer sensitivity be improved by an order of magnitude to measure the slower rate of growth of the 2-1/4Cr-1Mo steel at temperatures approaching those of the Nelson Curve (450 C)?

What is the equilibrium methane pressure in the bubbles, which is equivalent to asking, what is the carbon activity in the Q&T 2-1/4Cr-1Mo steel?

Where and how do the bubbles nucleate in weld-metal and base-metal?

Do welds undergo hydrogen attack more, or less, rapidly than the Q&T 2-1/4Cr-1Mo base-metal, and why?

Our work on each of these questions will be taken up in turn.

OILATOMETRY — Reproducible measurements were made at an order of magnitude lower strain rates (1.0 E-8/hr.), primarily through improvements in temperature control, since temperature fluctuations were the main source of variance not lack of sensitivity in the capacitance circuit.

CARBON ACTIVITY — If one believes the literature, mild over-tempering will remove all of the M_3C from the Q&T 2-1/4Cr-1Mo steel (1), and the activity of carbon in equilibrium with the remaining carbides will be so low (2) that the methane pressure in the bubbles will be greatly reduced. The rate of hydrogen attack should correspondingly be reduced by an order of magnitude by mild over-tempering. No one had ever measured the activity of carbon in Q&T 2-1/4Cr-1Mo steel at these temperatures, though Natesan and Kassner (3) had developed a technique for such alloys, and used it at higher temperatures. Their technique involved equilibrating a steel sample with a pure Ni foil, then measuring the carbon content in the nickel, and from that calculating the activity of the carbon in the 2-1/4Cr-1Mo steel.

We have used this technique to measure the carbon activity of Q&T 2-1/4Cr-1Mo steel at 550 C. The activity vs. tempering parameter (TAP, define..) is shown in Fig. 1. On the same graph is drawn the steady-state rate of specimen growth (hydrogen attack). The longest tempering time here is over 100 times longer than the commercially specified tempering treatment for pressure vessel steel. Note that there is no drop in the activity of carbon, or the rate of hydrogen attack, with this excessive tempering.

STEM work carried out for us by Prof. R. Odette has shown that there is no detectable M_3C left in the Q&T 2-1/4Cr-1Mo after this treatment. Thus there is something seriously wrong with Geiger and Angeles' model of the activity of carbon for the more stable carbides in these low Cr steels. However, for the first time we know with certainty what the carbon activity and methane pressures are in this alloy steel, and can do much more reliable analyses of the mechanisms limiting the growth kinetics.

BUBBLE NUCLEATION — In any study of nucleation there is the problem of what happens to the nuclei between the time when they first form and the time when they can first be observed with the technique being used. This problem is still plaguing measurement of the nucleation rate of pores in creep studies.

Two types of observations led us to suspect that the nuclei for hydrogen attack bubbles already existed in the 2-1/4Cr-1Mo sample before the steel was exposed to hydrogen:

The dilatometer we have developed and used is so sensitive that with it we can follow the growth of bubbles long before they can be seen with the SEM. In following the kinetics of growth of 2-1/4Cr-1Mo under hydrogen attack conditions we have always noted that growth starts at a relatively rapid rate as soon as the hydrogen has a chance to diffuse into the steel. The rate then decreases over the next couple of days to a steady-state value.

The maximum (equilibrium) methane pressure that can form in tempered 2-1/4Cr-1Mo steel will only drive the growth of bubbles larger than about 0.05 microns. Nuclei this large will form spontaneously at only an extremely small rate, certainly not at the high initial rates required to fit the observations.

We have now shown with a TEM/replica technique that the pores that lead to bubbles in the hydrogen attack of 2-1/4Cr-1Mo steel exist at the tips of carbides formed during the tempering process. Attached as Appendix I is a paper recently published in ACTA MET (4) which describes these results. Two points of interest should be added to what is in the paper:

The number of bubbles per unit volume observed in the 2-1/4Cr-1Mo microstructure after exposure to hot hydrogen is a factor of 2 or 3 less than the void density in the original quenched and tempered steel, and stays constant during the continuation of hydrogen attack. That is, the majority of the voids formed by tempering sinter shut during the early stages of hydrogen attack, and no new bubbles nucleate.

These observations have subsequently been confirmed by Professor R. Odette (UC Santa Barbara) using very similar techniques.

Work on normalized carbon steel undergoing hydrogen attack indicates that the density of voids in the steel before exposure to hydrogen is much lower than in the Q&T 2-1/4Cr-1Mo steel, but in the carbon steel the density of bubbles increases, by a couple of orders of magnitude, to a level much greater than that in the 2-1/4Cr-1Mo steel during the early stages of exposure to hydrogen. Thus a fundamental difference between the rate of hydrogen attack of carbon steel and Q&T 2-1/4Cr-1Mo is the number of bubbles that form, and the way in which they form. In the carbon steel the methane pressure in the few pre-existing voids is enough to generate a dense array ($1.0 \text{ E}+7$ per sq. cm) of bubbles on the boundaries, while in the 2-1/4Cr-1Mo steel the lower methane pressure does not generate any additional bubbles during hydrogen attack.

WELD METAL vs. BASE METAL — We studied two different commercial welds, one made by submerged arc, and one by consumable electrode. (In addition

* Reprint removed.

W. Erwin (5) has studied an electro-slag-refined weld in 2-1/4Cr-1Mo.) We find that the initial void density is higher in the weld-metal (EM) than in the base-metal (BM), that the bubble density is higher in WM than BM after hydrogen exposure, and that the growth rates are higher for the welds than for the BM. In addition the WM produced by consumable electrode expands faster than that produced by submerged arc. This results in predictions of significantly lower allowable temperature limits for the WM than for the BM. Fig. 2 shows a suggested Nelson Curve for Q&T 2-1/4Cr-1Mo steel. (The rationale for this curve is given in Appendix II.) It is clear that the limit line for the WM must be lower than that for the BM, and we argue in APP. II that the limit line for the WM should be lower than that now given by the API's Nelson Curve (6).

It is also interesting to compare the lines in Fig. 2 for the two different weld metals. That for the consumable electrode WM is lower than that for the submerged arc WM. Erwin (5), using less sensitive techniques, but longer times, reported no difference between his ESR-WM and his base metal. Thus with three different WM's we get three different answers ranging from good performance (as good as the BM), to poor performance. The only reason we can give for this difference is the higher density of bubbles that develops in the poorer welds. In fact the consumable electrode WM developed pores throughout the grains, not just at the boundaries. This density was high enough that the bubble driven strain was primarily by creep of the grains, not by boundary diffusion driven expansion as in the BM. We have no idea what microscopic microstructural defects cause this higher bubble density, though one could speculate about it. The main problem with confirming such speculation is that the initial porosity that develops into bubbles is less than 0.1 microns in diameter, and thus not amenable to measurement by any standard technique.

KINETIC MODELS — The remaining significant achievement of this work is the production and testing of a new model for the interpolation and extrapolation of the kinetic data we have obtained, and for the predictions of curves of the type shown in Fig. 2. The main virtues of this model are, a decreased number of disposable parameters, and an ability to fit a wide range of the data well. For example, we have concluded that in 2-1/4Cr-1Mo steel the bubble density is not so low that Dyson's "cage" creep constraint of surrounding grains operates to restrain growth. Also, models have been developed for including power-law creep in the lattice surrounding arrays of bubbles on grain boundaries, and for bubbles uniformly distributed throughout the grains. The model is also of benefit for calculating the tensile stress that develops normal to the grain boundary between bubbles growing by boundary diffusion.

A paper is in preparation that describes the model in more detail.

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Figure 1: Plot of carbon activity, and growth rate (550°C and 20.3 MPa hydrogen), versus tempering parameter for Q&T 2-1/4 Cr-1Mo steel.

Figure 2: Suggested limit lines for the use of Q&T 2-1/4 Cr-1 Mo steel base metal, and weld metal made by different techniques. Appendix II discusses the approach used in arriving at these limit lines.

Publications

"Chemically Driven Cavity Growth," P. G. Shewmon, H. Lopez and T. A. Parthasarathy, Scripta Met. 17, (1983). 39-43

"Precipitation Induced Voids in Quenched and Tempered Steel," Hugo Lopez and P. G. Shewmon, Acta Met. 31, (1983) 1945-50.

"Kinetics of Methane Bubble Growth in a 1020 Steel," Binayak Panda and P. G. Shewmon, Met. Trans. A.,

"On the Nelson Curve for 2½ Cr-1Mo Steel", P. G. Shewmon, H. F. Lopez, T. A. Parthasarathy, - submitted to ASME for publication as the Proceedings of the 1984 Pressure Vessel and Piping Conference.

"Effect of Welding on the Hydrogen Attack Kinetics of 2½ Cr-1Mo Steel" T. A. Parthasarathy, H. F. Lopez, P. G. Shewmon - In preparation.

"Effects of Tempering on the Carbon Activity and Hydrogen Attack Kinetics of 2½ Cr-1Mo Steel", T. A. Parthasarathy and P. G. Shewmon - In preparation.

"Mechanisms of Hydrogen Attack of Carbon and 2½ Cr-1Mo Steel" T. A. Parthasarathy and P. G. Shewmon - In preparation.

"Bubble Nucleation During Hydrogen Attack of Steels", MingMei Wang, T. A. Parthasarathy, P. G. Shewmon - Presented at the TMS/AIME Fall 83 Meeting.

Ph.D. Theses

Binayak Panda - Spring Quarter 1982

"Kinetics of Hydrogen Attack in a 1020 Steel."

Hugo Ferreira Lopez - Autumn Quarter 1983

"Hydrogen Attack Mechanisms in a 2-1/4 Cr 1 Mo Welded Steel."

Triplicane Parthasarathy - Autumn Quarter 1983

"Kinetics of Hydrogen Attack of 2-1/4 1 Mo Steel."

*Appendix I (reprint) has been removed.
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APPENDIX II

ON THE NELSON CURVE FOR 2-1/4 Cr 1-Mo STEEL

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ABSTRACT

Recent work on 2-1/4 Cr 1-Mo steel by several different groups suggest that the last Nelson Curve published by the API needs to be updated. A procedure for combining the diverse experimental observations is suggested, and a revised Nelson Curve is presented. It is found that welds may fall significantly below the API curve for the base metal depending on the mode of manufacture.

ON THE NELSON CURVE FOR 2-1/4 Cr 1-Mo STEEL

P.G. Shewmon, H. Lopez, and T.A. Parthasarathy

The Nelson Curve (1) defines the recommended operating limits in temperature and hydrogen pressure for a given steel. This is based on a combination of industrial experience ("failures") and laboratory work, with much of the data being given as points on the published API curve. In the case of quenched and tempered (Q&T) 2-1/4 Cr 1-Mo steel the currently published curve shows one data point which suggests that the performance limit of the steel is based on decarburization and not the formation of methane bubbles. Several workers have now shown that indeed copious quantities of methane bubbles form and grow in relatively short times at temperatures near and above the Nelson curve, that is 450°C at $P_{\text{H}_2} > 2 \text{ Ksi}$ (2-12). A Japanese program (2-4) at 600°C (29 MPa hydrogen, 1000 to 4000 hr) found a reduction in ductility and toughness, as well as numerous though separated bubbles. Erwin (5) working at 450° to 540°C (7 to 21 MPa hydrogen, up to 5 yr) measured comparable bubble densities, but found little loss of properties in room temperature tensile test. Wanagel, et al (6) found that modest exposure to hydrogen (14 MPa, 600°C , 20 days) developed methane bubbles sufficient to materially reduced stress rupture life in subsequent tests at 600°C . Cuiffreda, et al (7) showed that 13.8 MPa hydrogen at only 455°C would decrease the ductility in a hot tensile test. Work by the authors (8-11) using metallography and a sensitive dilatometer (20 MPa, 475 - 580°C , up to 2000 hr) show that attack is clearly taking place in this temperature range, and that commercial welds can be attacked at much greater rates than the base metal. The studies clearly indicate that the limiting condition for using Q&T 2-1/4 Cr 1-Mo steel will not be decarburization but the loss of integrity through methane bubble growth. Thus a new effort to define the variables that determine the Nelson curve for this alloy is appropriate.

We have recently carried out careful, quantitative studies of the kinetics of the hydrogen attack (HA) of two heats, and two welds, of 2-1/4 Cr 1-Mo steel (10,11). These data, and the models developed to describe the data, provide a basis for proposing an improved Nelson curve. To do this we must develop answers to several questions:

- Under what conditions could decarburization play a significant role in the hydrogen attack of 2-1/4 Cr 1-Mo steel?
- Is the incubation time for the development of bubbles primarily determined by the nucleation or the growth of the bubbles?
- What should be used for a "failure" criterion?
- What equations can be used to extrapolate the short term laboratory data to the times of industrial interest?
- How does one allow for the inherent differences between various heats, heat treatments, and weldmetal vs. basemetal in arriving at an appropriate limiting curve?

DECARBURIZATION

The API Nelson Curve for 2-1/4 Cr 1-Mo steel suggests that decarburization sets an upper limit on the temperature for using this alloy. Decarburization occurs at the other surface, and is a slow process since it would require the diffusion of carbon through the steel for a distance of centimeters before it would have any real effect. The internal formation of methane bubbles is a competing decarburization process which requires carbon diffusion only over a distance of a grain diameter or micrometers. Thus though decarburization can occur in the temperature range (13), it would be the dominant factor in material degradation only under conditions where internal methane bubbles would not form, for example at low hydrogen pressure and high temperatures. Since we now know that methane bubbles will grow at 450°C at hydrogen

pressures over 2 Ksi it seems unlikely that decarburization would play a limiting role for most applications of Q&T 2-1/4 Cr 1-Mo steel.

If the formation of methane bubbles was copious enough that they link up and form given boundary fissures that vented to the free surface, these fissures could lead to the formation of a deeper decarburization layer. Such fissure diagonal venting is the source of the deep decarburization that can develop in cold worked carbon steel in a relatively short time (14).

INCUBATION TIMES

Whenever an incubation period exists for a process involving nucleation and growth, there is a question of which takes the longer time and thus determines the overall kinetics. To study the changes that occur in steel when it is first exposed to hot hydrogen, one needs quite sensitive techniques of microscopy to see the embryonic bubbles, or dilatometry to follow the growth of the bubbles. In a dilatometric study of the growth kinetics of Q&T 2-1/4 Cr 1-Mo steel between 500° and 540°C, and under 3 to 4 Ksi hydrogen, Yu and Shewmon (8) found that steel samples started expanding immediately upon exposure to hydrogen. Moreover, the rate of sample expansion decreased with time during an initial transient (40-60 hr) until a lower steady-state expansion rate developed. Essentially the same results have been obtained in subsequent work by Lopez (10), and Parthasarathy (11) using two other heats of 2-1/4 Cr 1-Mo and also in the weldmetals of these two sections from commercial pressure vessels. This leads to the hypothesis that there is no nucleation barrier to be overcome before bubble growth can begin, that no bubble nucleation occurs during the incubation time, and that bubble growth is the limiting process during the entire incubation period.

Two independent studies support this hypothesis. Lopez and Shewmon (15) have shown, using TEM/replica techniques, that a significant density of sub-

micron voids exist at the tips of many carbides in the weldmetal and basemetal of a 2-1/4 Cr 1-Mo pressure vessel immediately after the tempering required to meet the ASME code, i.e. at 690°C for 25 hr. The density of bubbles that develop following exposure to high pressure hydrogen was a factor of 2 or 3 lower than this initial void density. A careful metallographic analysis following long term hydrogen exposure has been reported by Erwin (5). (See Fig. 1a). He found that the number of bubbles per unit area on a polished section increased steadily with time. However, if instead of areal bubble density (N_s) we plot volumetric bubble density (N_v), where $N_v = N_s/2r$ and $2r$ is the average bubble diameter, we find that the number of bubbles per unit volume does not increase with time of exposure (see Fig. 1b) Lopez (10) has found the same using the more sensitive TEM/replica technique over a shorter period of time (Fig. 1b). Thus the development of bubble volume during HA is entirely limited by the growth of bubbles with no inhibition due to slow nucleation.

"FAILURE" CRITERIA & EXTRAPOLATION EQUATIONS

In carbon steel it is relatively easy to develop fissures during HA through the nucleation, growth, and link-up of bubbles along grain boundaries. However, in Q&T 2-1/4 Cr 1-Mo steel the bubble density does not increase with time (Fig. 1), so fissures do not develop, and the room temperature tensile mechanical properties are relatively little affected even after the volume of bubbles exceeds that corresponding to severe degradation in carbon steel ($dV/V = 1E-3$). Though Erwin (5) reported little change in tensile ductility at $dV/V = 1E-3$, we will take it as our "failure" criterion for the following reasons:

- Erwin reported that the rate of bubble volume growth was increasing in this range (5).
- This bubble volume is enough to materially decrease the creep ductility (6,7).

- The impact strength is materially reduced in this range of bubble volume (2).

Extrapolation of kinetic data to longer times is simple because capacitance dilatometric studies show that after an initial incubation period the rate of linear expansion of the sample (dx/x) remains essentially constant until it approaches $dx/x = 3E-4$, or $dV/V = 1E-3$ (8-11,16-17). This approach was confirmed independently by Erwin (5) who measured the variation of the size and number of bubbles with time up to a total time of 5 years. From these data he calculated the linear strains after different times of exposures, and found that the strain rate remained fairly constant up to a dx/x of about $5E-4$. He also found that the strain rates obtained from his long term exposures were comparable to the equations that described Yu's (8) short term dilatometric data.

From these observations it is clear that the short-term dilatometric data can be used to predict the long-term effects up to strains of the order of $1E-3$. As a means of predicting the upper limit of safe use of 2-1/4 Cr 1-Mo steel we will assume the following:

- $dx/x = 3E-4$ as a strain limit.
- The strain should not occur in under 50,000 hr (6.2 yr).

These assumptions correspond to a minimum strain rate of $6E-9$ per hr.

From the dilatometric results the linear strain rates, $d\ln(x)/dt$, can be expressed in the form

$$d\ln(x)/dt = B (P + s) \exp(-Q/RT) \quad (1)$$

where s is the applied tensile stress, P is the equilibrium methane pressure, T is the absolute temperature, and B , n , and Q are experimentally determined constants (10,11). The equilibrium methane pressure can be calculated using

the equations derived by Odette and Vagarall (18,19) for the conversion of methane fugacity (f) to methane pressure (P), and the equations of Geiger and Angeles (20) for the carbide equilibrium constant. These are:

$$f = 1.84E-6 \exp(12,600/T) P \quad (2)$$

$$f = P \exp[P C(T)] \quad (3)$$

where, $C(T) = (1.19/T) + 3.09E T \quad 1E3 < f < 1E4$

$$= 0.005 \quad 1E3 > f$$

Solving these equations for a critical strain rate of $6E-9$ per hr determines the safe temperature/hydrogen pressure limits for the steel or weldmetal in question. Figure 2 plots these limits for the several heats of Q&T 2-1/4 Cr 1-Mo steel and weldmetal we have studied, and for $s = 15$ Ksi. This assumed applied stress could easily be present as a combination of the operating stresses in the system and residual stresses left from fabrication plus tempering. The figure also shows the Nelson Curves for the weldmetals without any imposed stress. The stress is seen to have little effect at the highest pressures but an increasing effect as the hydrogen pressure falls below 20 MPa (3 Ksi).

From Fig. 1 it is seen that the different basemetal heats behave quite similarly, while the two weldmetals differ significantly from each other. This suggests that the susceptibility to HA of 2-1/4 Cr 1-Mo steel weld is sensitive to the welding technique. Weld 1 was formed by a shielded metal arc technique while Weld 2 was formed by a submerged arc technique. Erwin (5) studied a weld made by an electroslag welding process, and reported no significant difference between the HA tendencies of weld and base metals. Thus, the different impurities introduced during the different welding processes can change the sensitivity to HA appreciably. The HA strain rate is very sensitive to the bubble density, in fact the differences in HA behavior

between carbon and 2-1/4 Cr 1-Mo steels have been shown to be largely due to the differences in bubble density that develop in the two steels (11). Sulfur may be the main impurity that causes the differences between the welds. Weld 1 had a somewhat higher S content than Weld 2 (0.0012 vs 0.008%) and a higher sulfide inclusion density could lead to a higher bubble density during HA. (This would be consistent with the arguments put forward by Hipsley (21,22) and Middleton (23) on the role of sulfur in nucleating the voids that limit creep ductility in this temperature range.)

BASIS FOR NELSON CURVE

The design criteria for pressure vessels for use with high pressure high temperature hydrogen must depend on the application, expected life, and design philosophy. Clearly the studies made to date indicate that the API's current Nelson Curve will not result in net section yielding due to loss of yield strength. However, there is a real question of the adequacy of the line in view of the very low creep ductility one would expect from long term operation in this range.

The most important question raised by our work, and Fig. 2, is the adequacy of the welds being put into service. Clearly there is appreciable variation in the performance of the different welds. It is equally clear that there is currently no good technical basis for judging what welding parameters influence long term weld performance. We believe that the important parameter is the density of submicron pores that develop in the weldmetal but neither we nor anyone else understands what determines this density.

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FIG 1: Metallographic data of Erwin(5) and Lopez(10) on methane Bubble densities as a function of total sample expansion.
(a) Areal density (b) Volumetric density

FIG 2: Calculated 'Nelson Curves' for Several Heats and Welds of 2½Cr-1 Mo Q & T Steel.