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Hydrogen Compatibility of Structural Materials for Energy Storage and Transmission Applications

(Semiannual Report for Period Through January 15, 1976)

S. L. Robinson, A. J. West, H. J. Saxton

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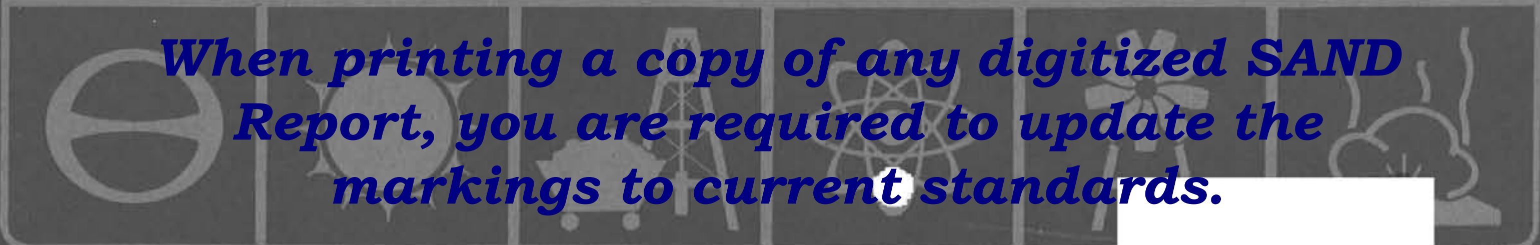

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HYDROGEN COMPATIBILITY OF STRUCTURAL MATERIALS FOR ENERGY STORAGE AND TRANSMISSION APPLICATIONS

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Sponsored by
ERDA Division of Conservation Research and Technology

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ABSTRACT

Work on the hydrogen compatibility of structural materials for pressure vessels and pipelines is proceeding along several fronts. In support of Brookhaven National Laboratories (BNL), the tensile behavior of a number of carbon and pressure vessel steels in high pressure hydrogen gas and in contact with iron-titanium hydride has been characterized. Slow crack growth studies of pressure vessel steels are nearing completion. Studies addressing the protective value of brush electroplated coatings are being continued. A new silicon coating applied by vapor deposition is also under study. Self-loaded tensile specimens are being prepared for use by BNL in an in-situ accelerated test program. Efforts are underway to modify the hydrogen compatibility of manganese-carbon and high carbon steels by thermomechanical treatment, and to characterize their mechanical properties and microstructures. The effects of chemical segregation on hydrogen cracking are also being studied. Construction of the experimental hydrogen pipeline is proceeding satisfactorily with initial safety tests to be performed soon.

CONTENTS

ILLUSTRATIONS

TABLES

HYDROGEN COMPATIBILITY OF STRUCTURAL MATERIALS FOR ENERGY STORAGE AND TRANSMISSION APPLICATIONS

INTRODUCTION

Many of our efforts supporting Brookhaven National Laboratories hydride storage program are now nearing completion. The screening tensile tests of structural steels have been completed. Slow crack growth studies will be completed by April when the extended compact tension specimens containing welds are removed from their exposure to high pressure hydrogen. Tests of the potential damage by direct hydrogen injection into metals due to intimate contact with $FeTiH_x$ have also been completed. A set of self-loaded tensile specimens have been ordered by BNL from Sandia for testing during accelerated hydride-dehydride cycling studies. The specimens are being machined, and loading fixtures are ready. Upon receipt of the specimens, they will be loaded and shipped to BNL for placement into the test vessel.

The construction of the pipeline loop is proceeding on schedule, as are the supportative materials programs. The pipeline site construction has been completed, major pipeline components are now being fabricated, and instrumentation for monitoring pipeline functions is being assembled.

A number of alloy characterization and development efforts have been underway since the last report filed. The effects of chemical segregation upon hydrogen compatibility are being studied. Mechanical properties resulting from thermomechanical treatments, such as warm working and high energy rate forming (HERF), have been studied and compared to annealed and cold worked properties. Programs to study the effects of alloy additions such as rare earths and silicon on hydrogen compatibility will begin soon. In addition, protective coating schemes continue to be explored, with brush plating studies continuing, and a new silicon coating produced by pyrolysis of silane being investigated.

HYDRIDE STORAGE SUPPORT

A summary of tensile tests in high pressure hydrogen was presented in the last report, SAND75-8040. Since then, additional tensile tests have been performed on A516 and A106 steels, after exposure to both $FeTiH_x$ and low pressure H_2 gas. The purpose of these tests was to determine if direct hydrogen injection by contact with $FeTiH_x$ could cause significant embrittlement. The results and test conditions are summarized in Table I. Long-term exposure to 1 atmosphere of H_2 gas (which produces a large internal hydrogen concentration) caused greater ductility loss than the exposure to $FeTiH_x$, when ductility is measured as % reduction of area. Testing in one atmosphere of H_2 is essentially equivalent to any effects due to direct injection of hydrogen by $FeTiH_x$. If it is assumed that only a monatomic layer of $FeTiH_x$, in contact with the metal, can inject hydrogen; then this amount is small. The tensile test results are consistent with such a mechanism.

A major new activity is the direct order placed upon Sandia by Brookhaven National Laboratories for a series of self-loaded tensile specimens. These specimens are to be placed in an $FeTiH_x$ bed and subjected to accelerated hydride-dehydride cycling. At the end of a simulated three years of service they will be removed, inspected, and tested to failure in air. The design of the specimen is shown in Figure 1. A tensile load is applied through the fixture and upper specimen threads by an Instron machine. A modified extensometer has been designed; it will be clamped to the gage length, reading tensile strain directly. By tightening the load nut and allowing for relaxations, the strain and hence the specimen load may be obtained directly and reproducibly. The test matrix is tabulated in Table II. Duplicate specimens of the preferred alloys A516 Grade 70 and A106-B are being tested (see the semi-annual progress report through June 30, 1975, SAND75-8040). Note that changes have been made from the matrix given in the last report. These changes are the result of information gathered since that report, and of a more developed design philosophy. The effect of protective coatings on the performance of smooth, notched, and notched weld specimens is a critical part of the test matrix. Alloys 6061-T6 aluminum and 304 stainless steel are included as reference points, since their behavior in hydrogen is well characterized.

Slow crack growth studies, begun last summer, are nearing completion. Extended compact tension specimens (described previously) of unwelded material have been exposed to 4.4 MP_a (600 psig) H_2 for seven months at stress intensities up to 88 $MPa\sqrt{m}$ (80 $ksi\sqrt{in}$). The specimens will be removed soon, fatigued to mark any existing slow crack growth, fractured, and examined. Similarly, the welded specimens will be removed from the test chambers in about six weeks. Remote monitoring of the stress intensities has suggested some crack growth in 2-1/4 Cr - 1/2 Mo and 4340, but the same indications can also result from partial detachment of the strain gauges from the specimens. To date, there has been no indication of slow crack growth in any of the other unwelded materials, A515 Grade 70, A516 Grade 70, 4340, A106-B, and C-95. No crack growth is indicated in welded A106-B, A515 Grade 70, and A516 Grade 70 in five months of exposure.

PIPELINE LOOP CONSTRUCTION

Photographs of the completed site including the instrumentation trailer are shown in Figure 2. Major pipeline components, including pipeline segments and the circulating pump housing are now being fabricated by outside contractors. To help insure safety of our experimental operations, the chemistries of all structural materials used in the pipeline loop are being certified back to their melted ingots and a detailed welding and nondestructive test specification has been developed at Sandia for this application.

A schematic layout of the site is shown in Figure 3, and the test module to be used in the pipeline is shown in Figure 4. The annular space in the test modules will be backfilled with inert gas so that any ruptures occurring in the thin test sections will not compromise other tests in progress in the pipeline. The modules are fitted with an instrumentation port to allow us to monitor slow leaks, potential ruptures, and permeation as needed. Multi-channel data acquisition units, with alarms in the event of an inner liner rupture, and recording devices to monitor pressure in the annulus will be operated. An oxygen detector will be operated continuously inside the pump chamber (for safety considerations).

Prior to actual assembly of the pipeline, a set of safety-oriented tests are planned. Three sections of flawed pipe will be hydrogen charged to simulate service conditions, and then burst with nitrogen gas. The purpose of this test series is to discover and protect against unsafe design features. Initially two modules of the design shown in Figure 4 will be constructed and installed in the line.

ALLOY CHARACTERIZATION

Warm Working

Alloys A515 and A516 were warm worked in an experimental sequence involving one hour at 1100°C, four 10% reductions while cooling to 600°C, and four 5% reductions at 600°C with one minute holds in the furnace between rolling passes.

Comparisons have been made between the mechanical behavior of warm worked and mill finished mild steels. This comparison is summarized in Figure 5, showing that a significant ductility improvement (%RA) may be obtained in the manganese-carbon pressure vessel steels A515 and A516. The sources of that ductility improvement may be seen to derive primarily from microstructural changes due to the warm working. Microstructures obtained prior to and after warm working are shown in Figure 6. Grain refinement, texture formation, partial spherodization of cementite and probably some subgrain formation result from the warm working process. There are positive suggestions in the literature that low angle boundaries, fine grain size, and dislocation networks all contribute to improved hydrogen resistance (References #1, 2, and 3). Spherodization has not yet been shown to be unequivocally beneficial, and the reduced scale of the carbides may play a more significant role in the net response to hydrogen.

Preliminary studies using the X-ray dispersive analyzer on the scanning electron microscope suggest that chemical segregation of alloying elements may also play a contributory role in hydrogen susceptibility. Banded structures such as the A516 in the as-received condition showed manganese enrichment in the pearlite colonies, and manganese gradients away from the pearlite into the bulk ferrite. Ferrite lamellae in pearlite were found to be similarly enriched. As received, the more equiaxed A515 showed significantly less segregation. Warm working of these alloys was found by dispersive analysis to have reduced the indicated segregation to very low values.

Surface cracking occurred in hydrogen tensile tests of the as-received A515 and A516 alloys at the pearlite - bulk ferrite interfaces. Less surface cracking was observed during similar tensile tests performed on warm worked materials. Whether this difference in performance results from microstructural or segregation effects is not yet clear. More detailed analyses are currently underway.

Fracture surfaces of the A515 and A516 have been compared in warm worked and mill finished conditions (See Figures 7A and 7B). Warm working reduces the dimple size of both A515 and A516 when tensile tested in air. In addition, fracture surfaces of the warm worked materials tested in hydrogen exhibit more ductility than their mill finished counterparts.

High Carbon Steels

Warm worked high carbon steels (1.3 w/oC) supplied by Prof. O. D. Sherby(4) of Stanford University have been tensile tested in high pressure hydrogen. These results are summarized in Table II. The maximum loss in ductility is 44% which is comparable with the mild steels. However, there is great variability of ductility among the samples tested in identical conditions, suggesting that inherent variability of metallurgical structure and the presence of flaws is as important as the exposure to hydrogen.

HERF Steels

Preliminary comparisons of high energy rate formed (HERF'ed) 1018, annealed 1018 and cold worked 1018 have been performed. Initial results have been mixed, i.e., the yield strength has been doubled and the ultimate strength increased by 30%. However, ductility losses in hydrogen remain high. Further comparisons must await more experimental results.

Rare Earth Modified (REM) Steels

Experiments on rare earth modified mild steels are still in the planning stage. The anticipated benefits of rare earth additions stem primarily from inclusion shape control. When coupled with thermomechanical treatments, good longitudinal and transverse properties in hydrogen are anticipated.

COATING DEVELOPMENT

We have examined the quality of controlled motion vs. manually applied brush electroplated coatings at various current densities. Optimum coatings were obtained at low densities (500 amps/ft^2) with mechanically controlled motion. A typical series of microstructures produced by both methods is shown in Figure 8 for a tin coating. Permeation measurements were performed only on the optimum coatings.

Lead was thought to be a desirable material to test since (1) the 70% Sn - 30% Pb coating was highly successful, and (2) tin itself was not found to produce low permeabilities. It was, therefore, suggested that lead might in fact be responsible for the performance of the alloy. As may be seen in the permeability plot of Figure 9, the explanation is more complex, since the permeability of lead is high. The reasons for the effectiveness of the 70% Sn - 30% Pb coating must lie in metallurgical structure and electroplating characteristics of the alloy itself.

An experimental silicon coating is being tested for its hydrogen permeability. Silane gas was decomposed at 425°C and 600°C onto a 1017 steel substrate producing 100A° and 1200A° thick coatings, respectively.

(Thicknesses were determined by Auger sputtering.) Extrapolating the permeability to room temperature for the 100A° coating, a 10^5 decrease is predicted. The 1200A° coating appears to have cracked, and gives only a small permeation reduction. Studies of the temperature and pressure dependence of the silicon coatings are continuing, in order to determine the rate controlling mechanism of permeation. Since it may have applications to large hardware, further silicon coating work is planned.

TABLE I. Comparison of Tensile Properties After Exposure to $FeTiH_x$ and 1 Atmosphere H_2 Gas

A516	Test	0.2% Yield	ULT Strength	RA	Uniform Elongation	Total Elongation
	Air	305 MPa	518 MPa	72.6%	20.8%	47.0%
	H_2	312	520	72.6	18.6	28.5
	Hydride Charged	306	512	72.6	16.7	27.6
*	H_2/48 hrs.	287	507	66.7	21.4	30.7
A106	Air	300	524	67.2	20.1	39.0
	H_2	312	531	64.2	17.7	25.4
	Hydride Charged	312	527	65.2	18.2	24.7
	H_2/48 hrs.	308	517	62.8	19.0	27.6

* Different Lot of A516 Material

H_2: Test in 1 Atmosphere H_2

Hydride Charged: Baked 72 hrs in $FeTiH_x$, and 1 atm. H_2, 72 hrs @200°C.
Tested in environment at room temperature

H_2/48 Hrs: Soaked 48 hrs. in 1 atmosphere H_2 prior to test.

TABLE II - Test Matrix for Long-Term In-Situ Self-Loaded Tensile Specimens

Condition	Material						
	A106 Proof Stress	A106 Design Stress	A516 Proof Stress	A516 Design Stress	6061 Proof Stress	Cr-Mo Proof Stress	304 Proof Stress
Smooth Matrix	2	2	2	2	2	2	2
Notch Matrix	2	2	2	2	2	2	2
Smooth Weld	2	2	2	2	2	2	2
<u>Notched Weld</u>							
Heat Affected Zone	2	2	2	2	2	2	2
Fusion Zone	2	2	2	2	2	2	2
<u>Coated (Sn-Pb)</u>							
Smooth Weld	2	1	2	1		2	
Notched Weld	2	1	2	1		2	

TABLE III - Tensile Data Warm Worked 1.3% C Steel

Charge	Test	0.2% Yield Strength	Ultimate Strength	%RA	% Uniform Elongation	% Total Elongation
Uncharged	Air	972 MPa	1034 MPa	15.1	11.0	18.3
Charged	Air	696 MPa	929 MPa	10.6	7.1	7.1
Uncharged	6.9 MPa H_2	796 MPa	1028 MPa	12.6	10.7	10.7
Charged	6.9 MPa H_2	800 MPa	986 MPa	8.5	6.7	6.7
Uncharged	69 MPa H_2	700 MPa	929 MPa	10.6	7.1	7.2
Charged	69 MPa H_2	836 MPa	916 MPa	10.1	5.8	5.8

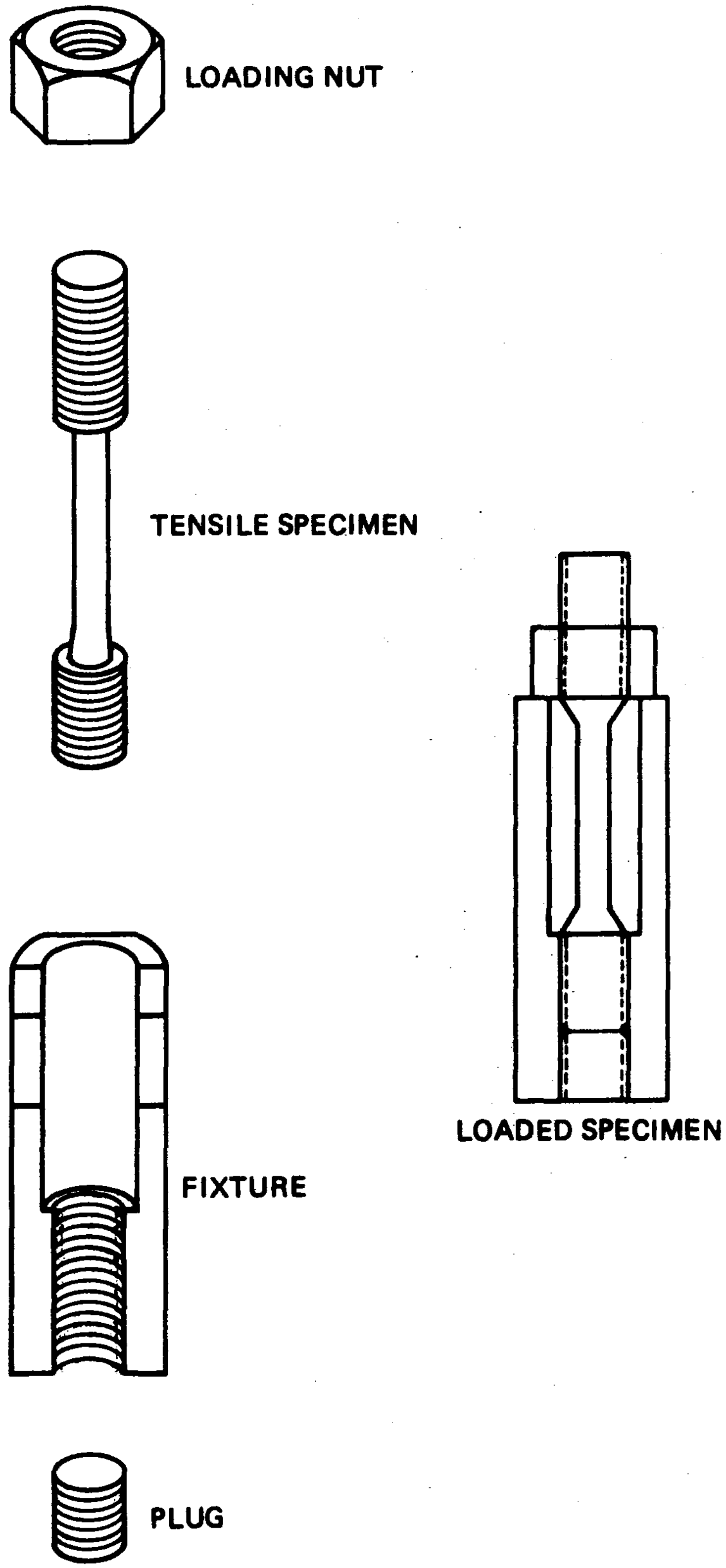

Figure 1. Self-Loading Test Specimen

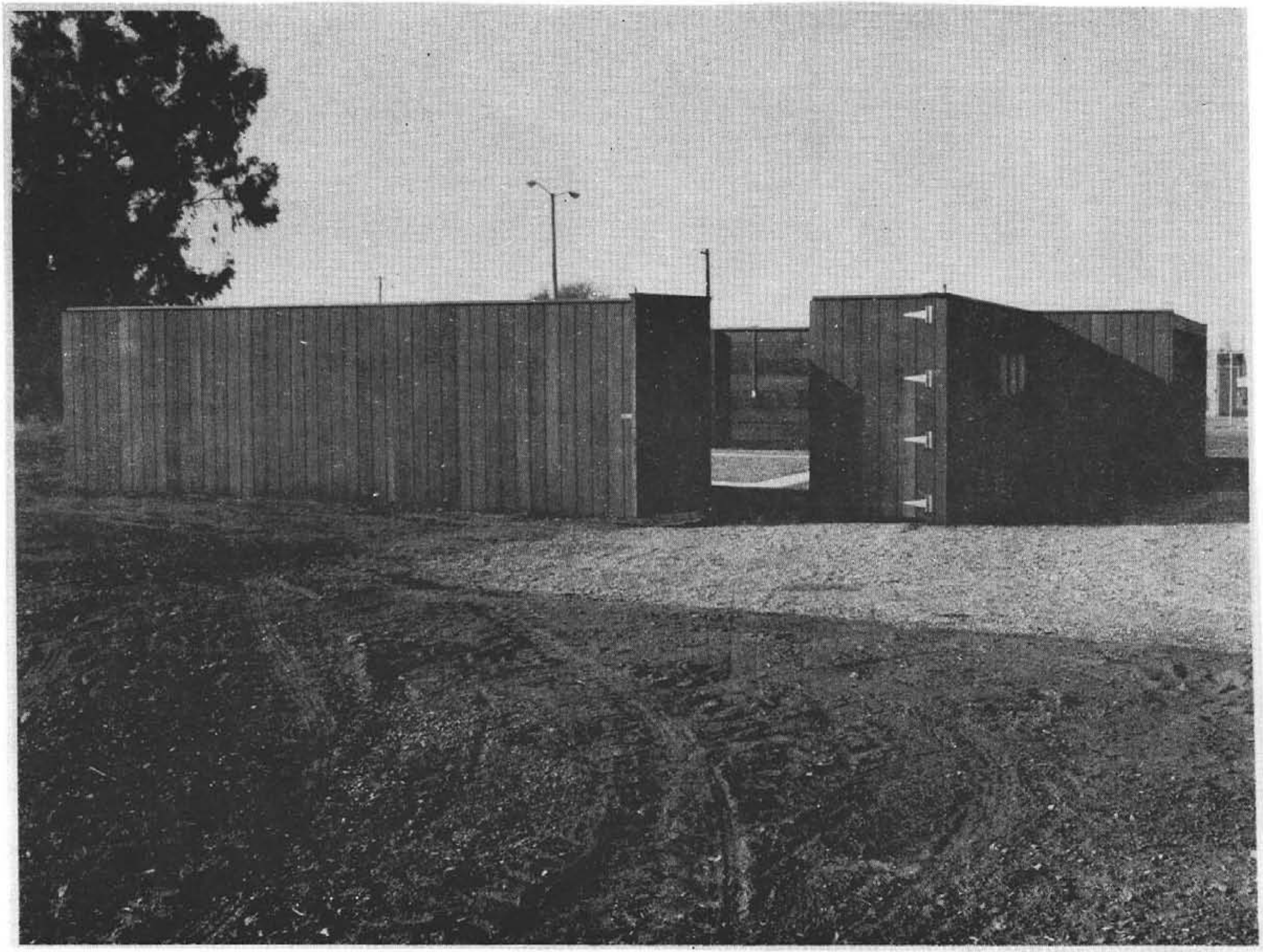

Figure 2A. Exterior of Site Showing Redwood Fencing.

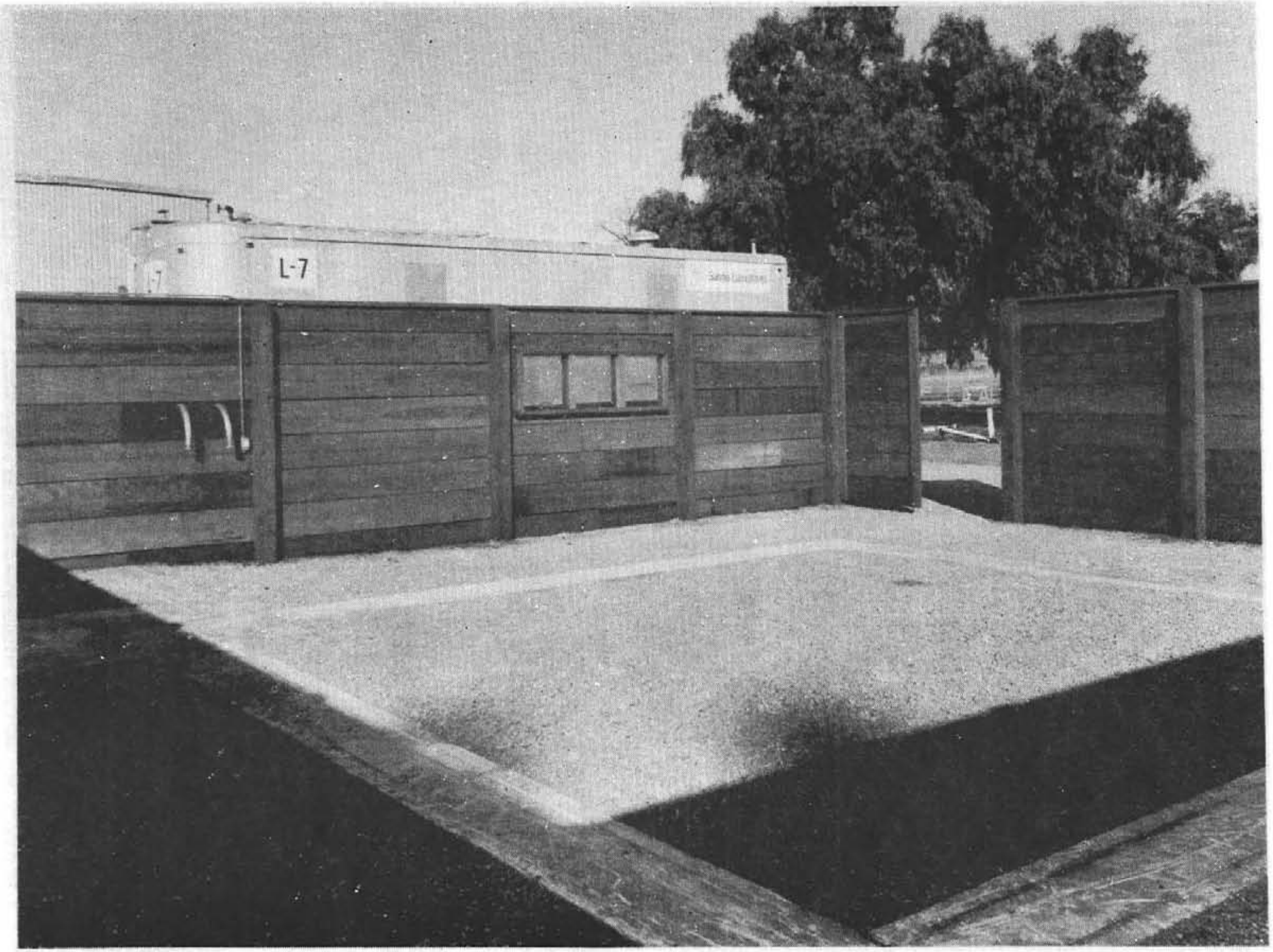

Figure 2B. Interior of Site. Instrumentation Trailer Beyond Fence.

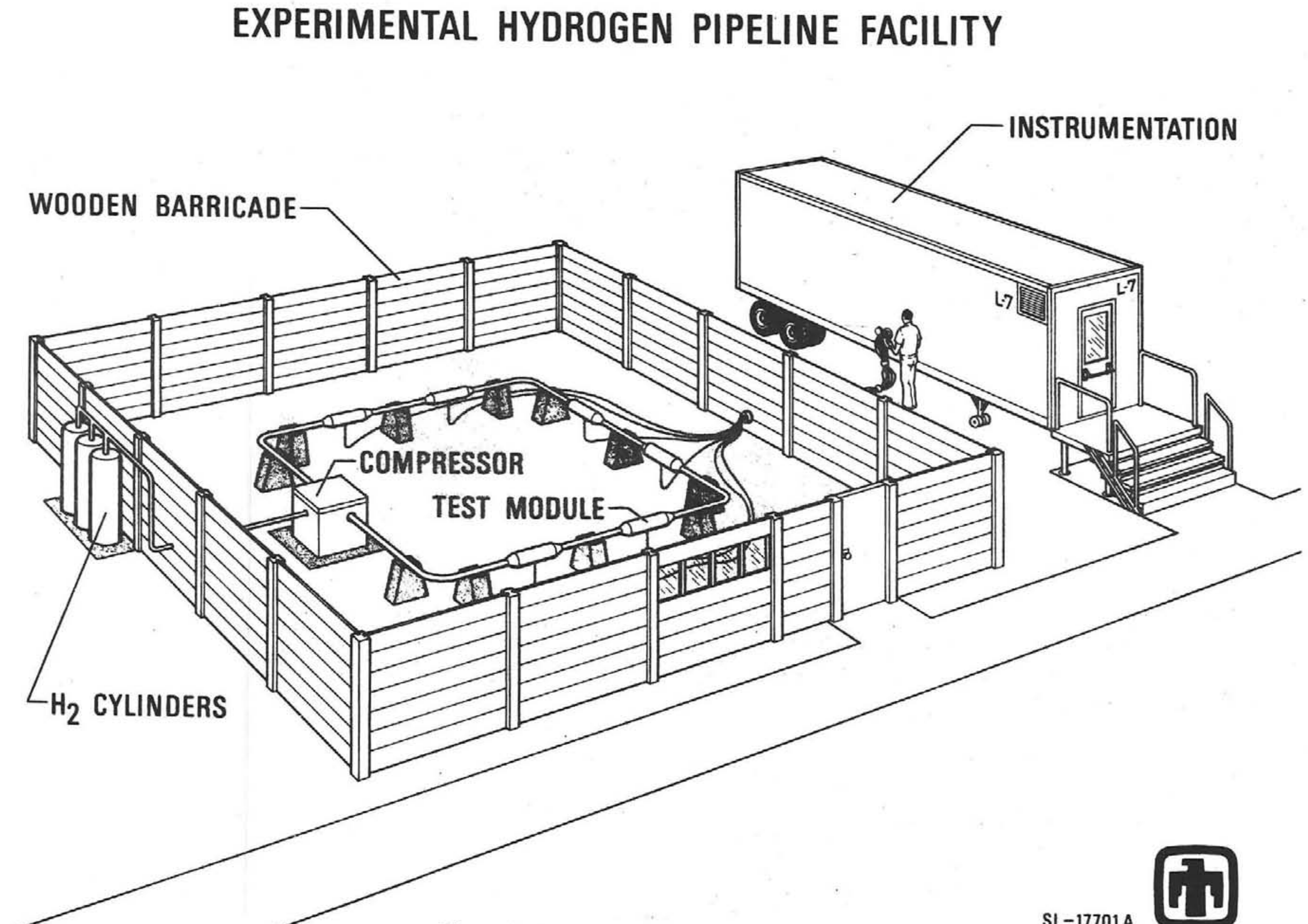

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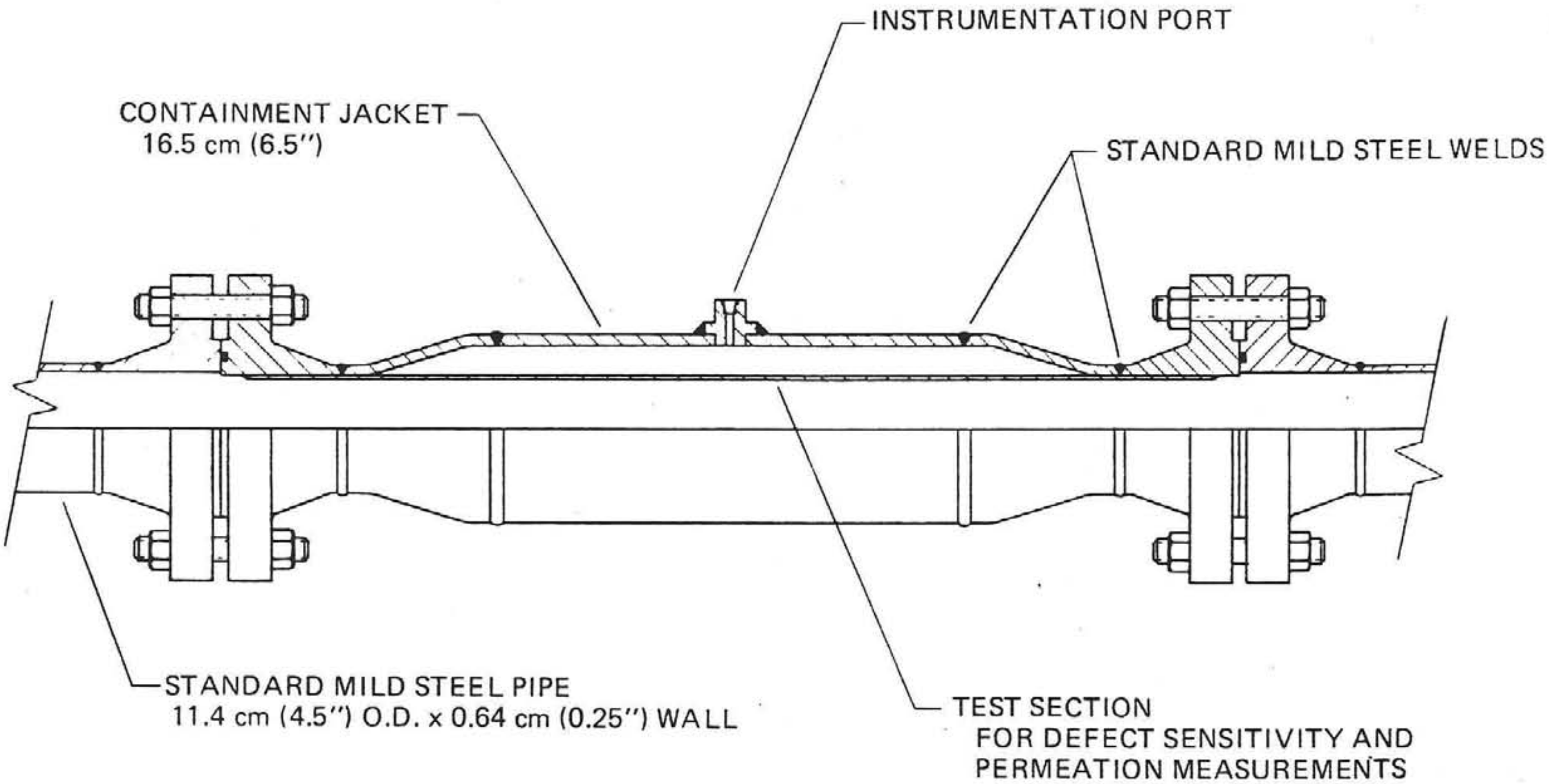
Figure 3. Experimental Hydrogen Pipeline Facility

MODULAR SECTION OF PIPELINE



DESIGN INFORMATION

*HYDROGEN GAS PRESSURE = 6.9 MPa (1000 psi)

*ALL MILD STEEL CONSTRUCTION

*MATERIAL STRESS LEVELS ≈ 25% of YIELD STRENGTH
(EXCEPT TEST SECTION ≈ 75%)

Figure 4. Modular Section of Pipeline

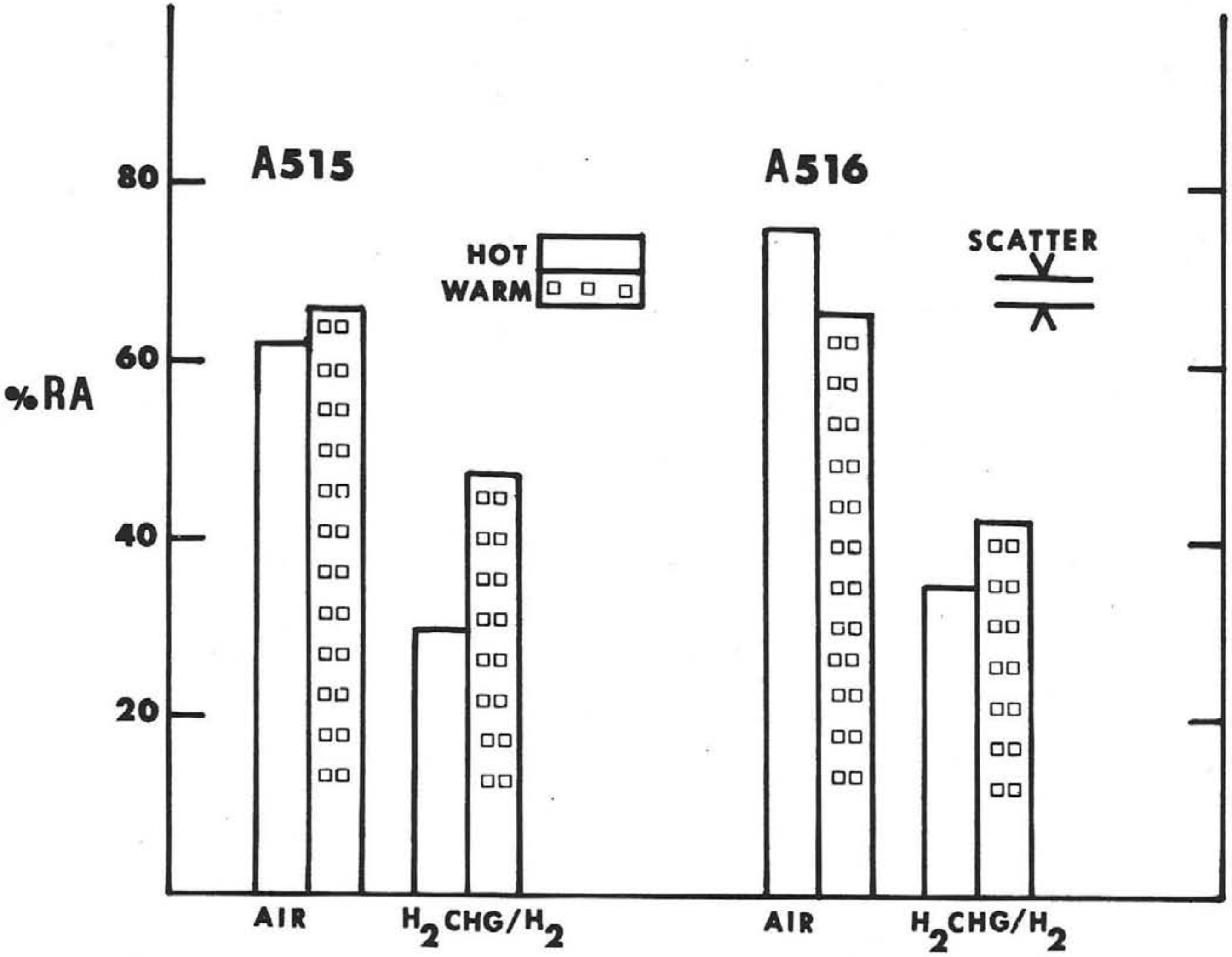
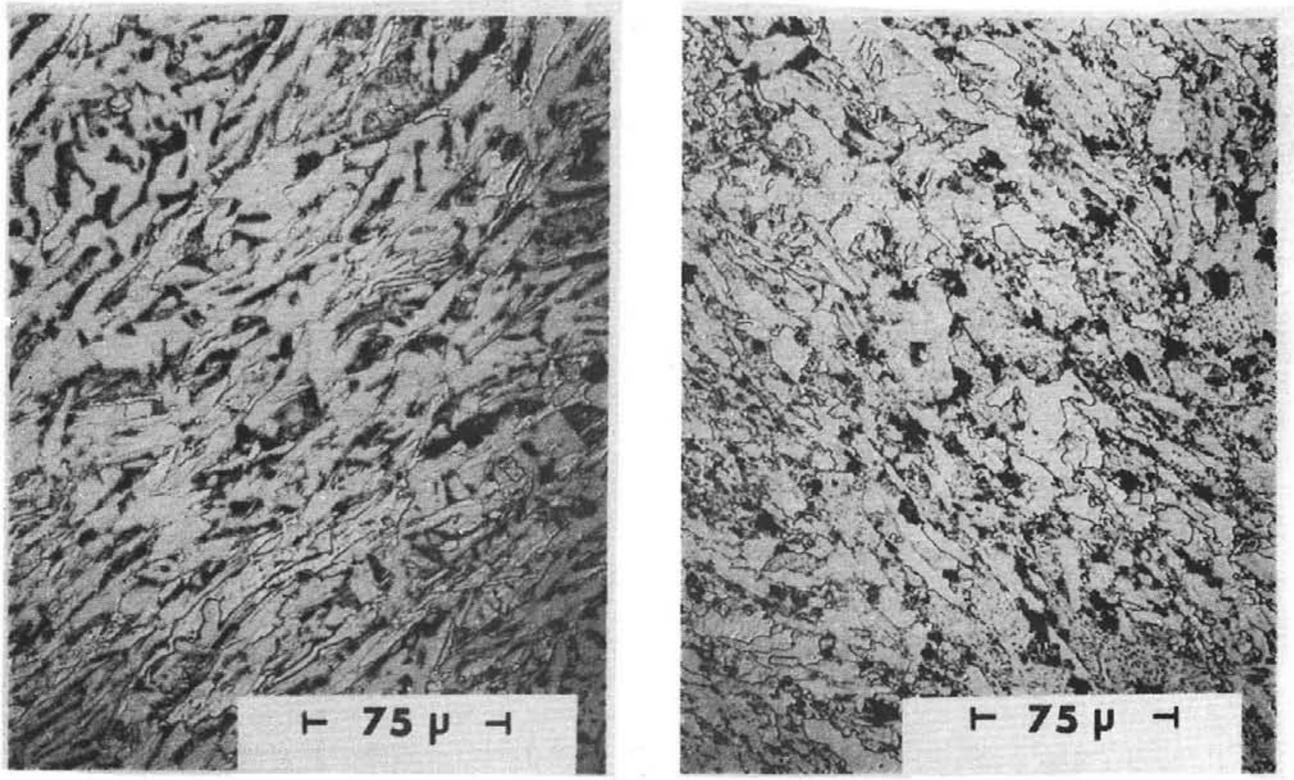
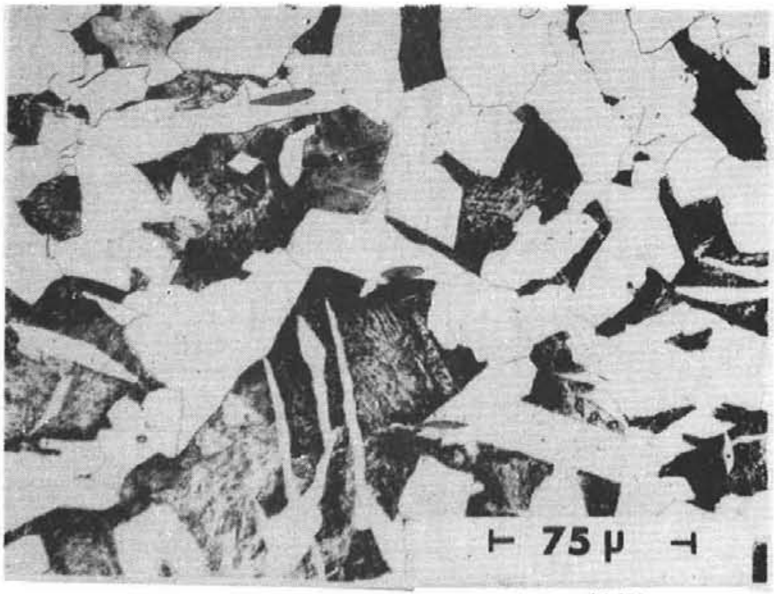


Figure 5. Influence of Warm Rolling on Hydrogen Compatibility of Pressure Vessel Steels



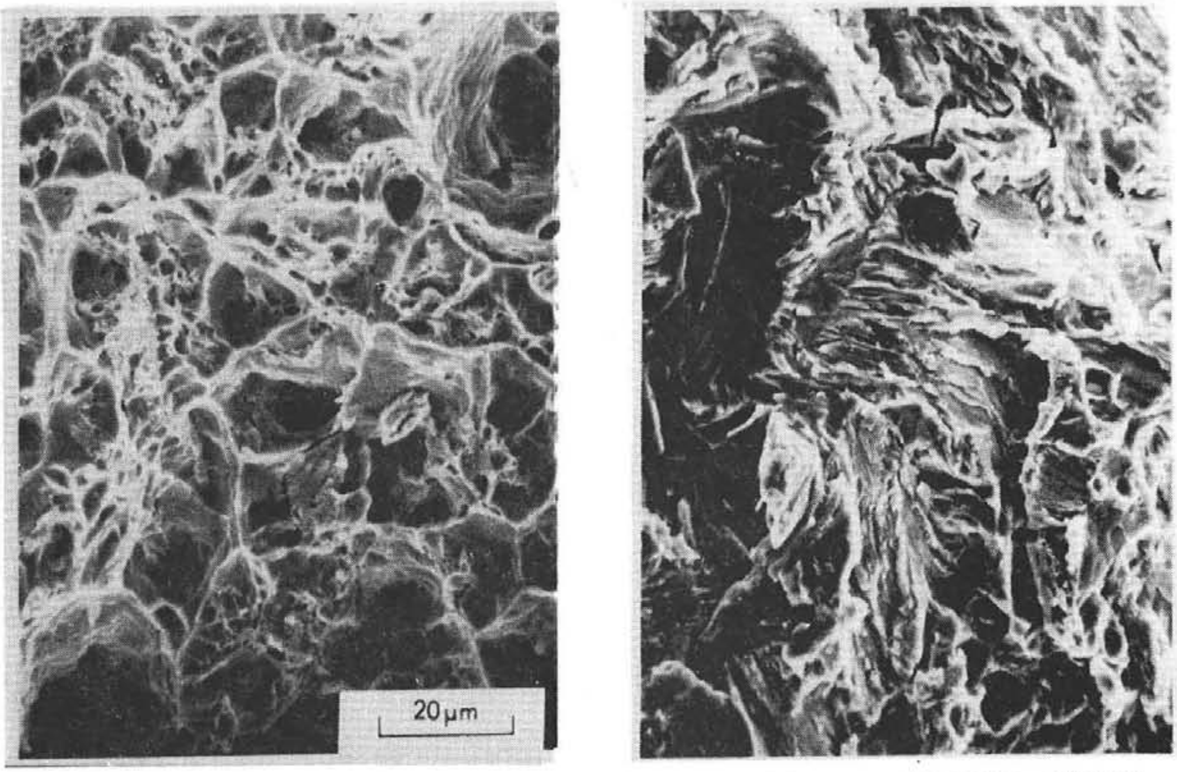
A516 **After warm working** 400X

A515 **After warm working** 400X



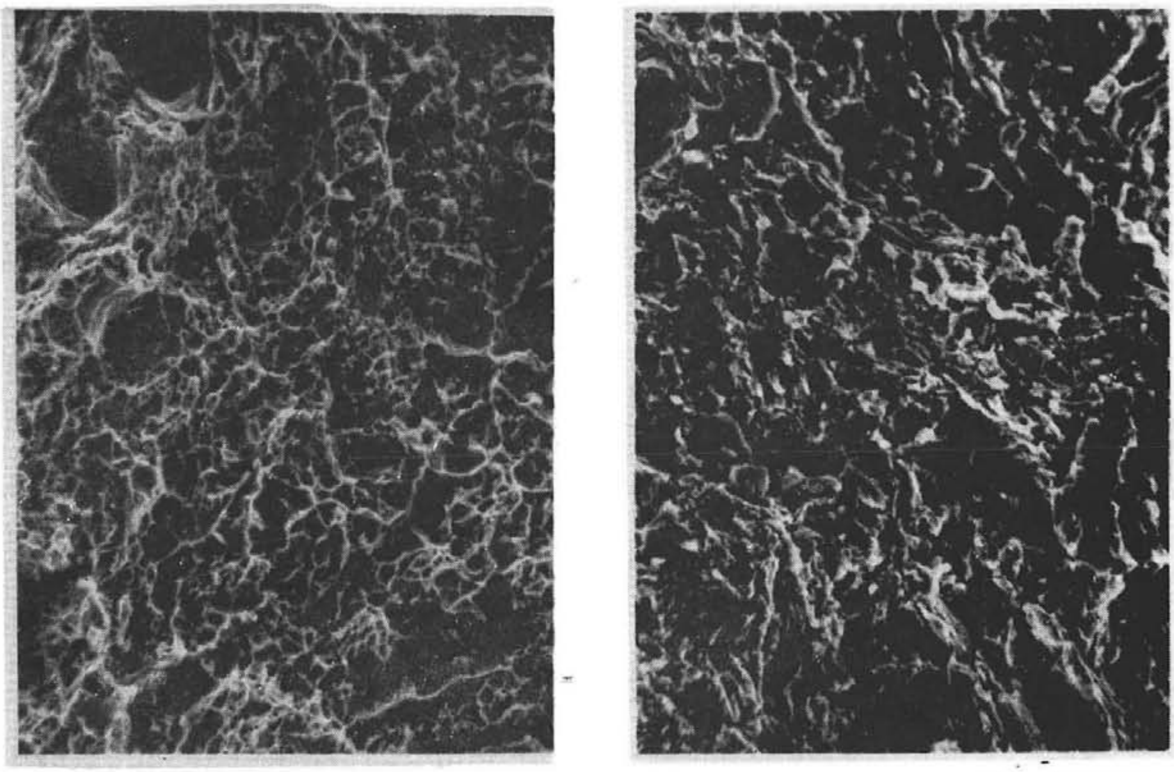
A515 **Before warm working** 400X

Figure 6. Microstructure Modification of A515 and A516 Steels by Warm Rolling



HOT ROLLED
UNEXPOSED TO H

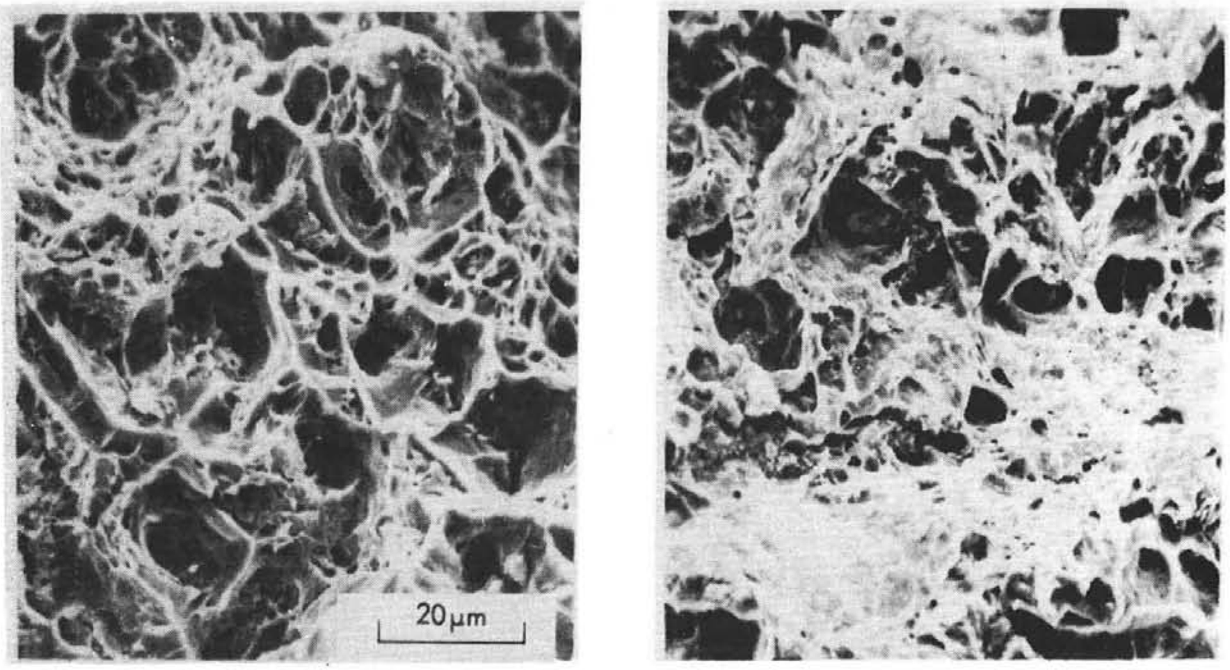
HOT ROLLED - THERMAL CHARGE
4.14 MPa H_2 TEST



WARM ROLLED
UNEXPOSED TO H_2

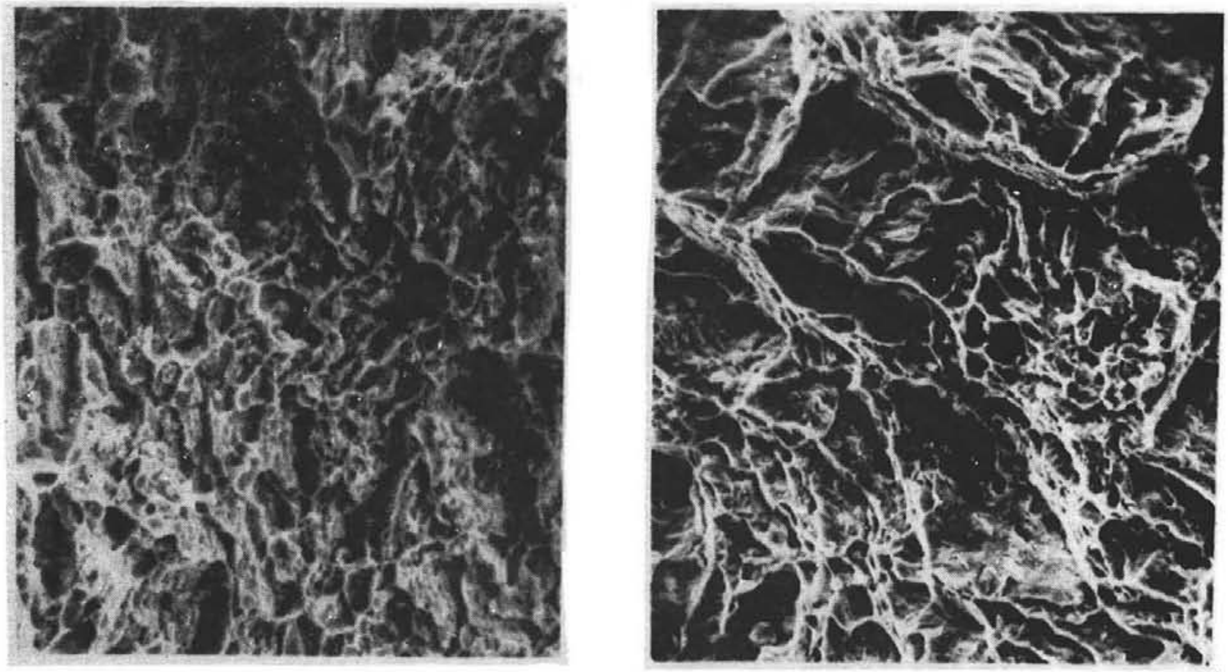
WARM ROLLED - THERMAL CHARGE
4.14 MPa H_2 TEST

Figure 7A. Fracture Surfaces of Mill Finished and Warm Rolled A515 Steels.



HOT ROLLED
UNEXPOSED TO H_2

HOT ROLLED - THERMAL CHARGE
4.14 MPa H_2 TEST



WARM ROLLED
UNEXPOSED TO H_2

WARM ROLLED - THERMAL CHARGE
4.14 MPa H_2 TEST

Figure 7B. Fracture Surfaces of Mill Finished and Warm Rolled A516 Steels.

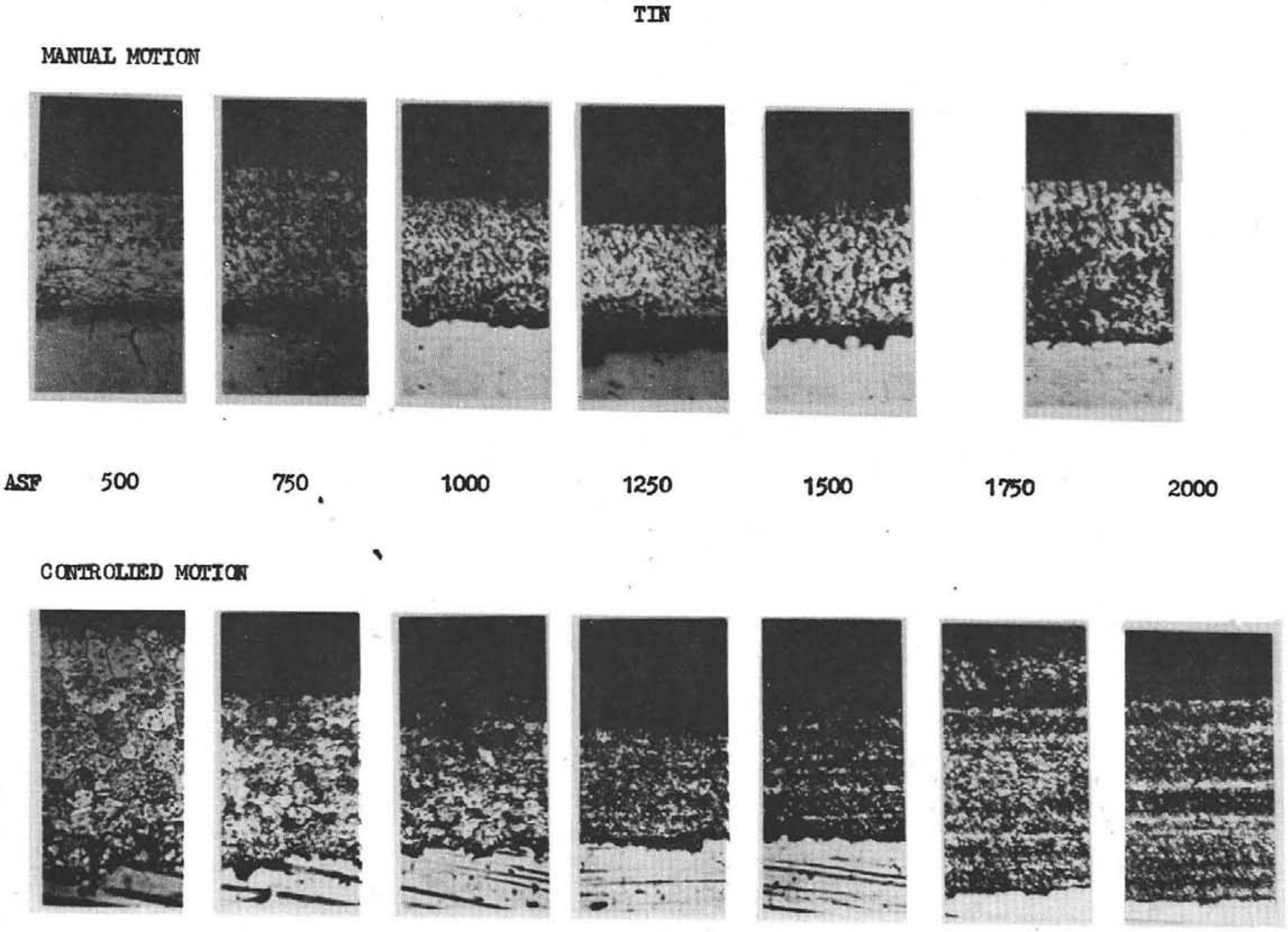


Figure 8. Controlled Motion vs Manual Motion Tin Plating Studies.

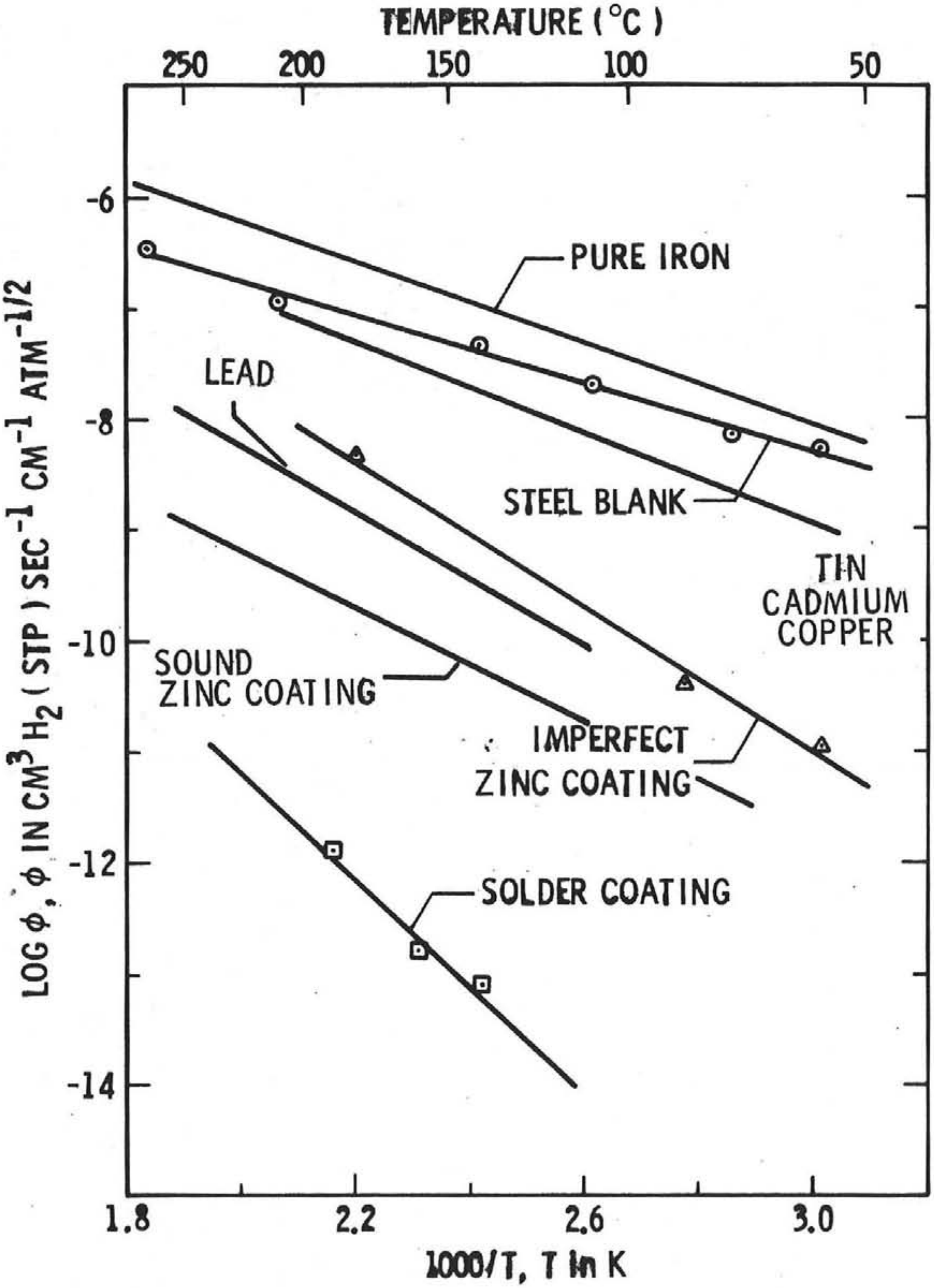


FIGURE 9. BRUSH PLATING AS A MEANS OF REDUCING HYDROGEN UPTAKE AND PERMEATION IN STEELS

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