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THE RESISTANCE OF SELECTED HIGH STRENGTH
ALLOYS TO EMBRITTELEMENT BY A HYDROGEN ENVIRONMENT

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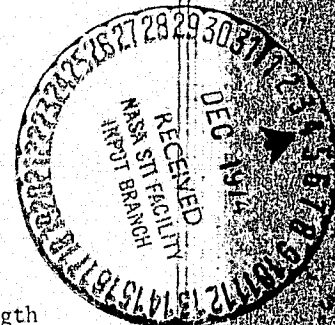
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ABSTRACT

Selected high strength iron base and cobalt base alloys with yield strengths in the range of 1233 to 2129 MNm⁻² (179-309 KSI) were resistant to degradation of mechanical properties in a one atmosphere hydrogen environment at ambient temperature. These alloys were strengthened initially by cold working which produced strain induced ϵ' -hcp martensite and fcc mechanical twins in an fcc matrix. Heat treatment of the cobalt base alloy after cold working produced carbide precipitates with retention of an hcp epsilon phase which increased the yield strength level to a maximum of 2129 MNm⁻² (309 KSI). High strength alloys can be produced which have some resistance to degradation of mechanical properties by a hydrogen environment under certain conditions.

INTRODUCTION

High strength martensitic and ferritic iron base alloys usually are embrittled by a hydrogen environment at substantially reduced stress or stress intensity levels in comparison to the maximum observed levels in an inert environment(1-3). High strength nickel base and titanium base alloys can be embrittled in a hydrogen environment under certain conditions(3). The chemistries and metallurgical microstructures of the alloys are selected to produce high strength, then the resistance of the alloy to embrittlement by hydrogen is determined. By investigating the relationship of alloy chemistry and metallurgical microstructure to hydrogen assisted cracking in simple alloy systems with a face centered cubic matrix, it may be possible to design high strength alloys which have some



resistance to degradation of mechanical properties in a hydrogen environment under certain conditions.

Face centered cubic alloys which are unstable with respect to strain induced transformations have high work hardening rates and can be cold worked to produce yield strength levels of the order of 1380 MNm^{-2} (200 KSI) (4-6). The usual strain induced structures formed in fcc alloys are α' -bcc martensite, ϵ' -hcp martensite, and fcc mechanical twins (6-10). Yield strength levels in the range of $1725\text{-}2136 \text{ MNm}^{-2}$ (250-310 KSI) can be produced in some of these alloys which do not contain α' by subsequent heat treatment after cold working (11,12). If substantial amounts of α' martensite form in an iron base austenitic alloy during mechanical testing, it has been observed that a hydrogen environment can degrade the mechanical properties of the alloy even in a one atmosphere hydrogen environment in some cases (13-16). Cold worked high strength Fe-Mn base alloys with an austenitic matrix which were partially strengthened by ϵ' martensite and fcc mechanical twins were resistant to degradation of mechanical properties in a one atmosphere hydrogen environment at ambient temperature (6).

The objective of this investigation was to determine the effect of a gaseous hydrogen environment on the fracture behavior of cold worked high strength alloys as a function of alloy chemistry and metallurgical microstructure which were partially strengthened by ϵ' -hcp martensite and fcc mechanical twins in an fcc matrix. One of the alloys was studied at a substantially higher yield strength level which was produced by subsequent heat treatment after cold working.

EXPERIMENTAL PROCEDURE

The chemical compositions of the alloys employed in this investigation are presented in Table I. The Fe-Mn alloys were solution treated at 1125°C and the cobalt alloy at 1150°C .

Table I. Chemical Composition of Alloys in Weight Percent

Alloy	Fe	Mn	C	N	Cr	Ni	Co	W	Mo	Be
Co-Alloy	Bal	1.60	0.20	0.00	20.0	13.0	42.5	2.80	2.0	0.04
Fe-16Mn	Bal	15.9	0.08	0.40	18.0	5.5				
Fe-25Mn	Bal	25.2	0.29							

The Fe-16Mn, Fe-25Mn, and cobalt base alloys were cold rolled by the amounts listed in Table II. Magnetization measurements were carried out for the iron base alloys with a magnet operating at a field strength level of 15,000 oersteds and using α iron as a standard. Some cobalt alloy specimens were also heat treated at 925°F for 3-1/2 hours after cold rolling.

Table II. Mechanical Properties of Alloys

Specimen	Environment	Yield Strength $N \cdot m^{-2}$	Red. in area (%)	Total Elongation (%)	K_I $MNm^{-3/2}$	Crack Growth Rate $m \cdot s^{-1}$
Fe-16Mn C.W.50%	Air	1391	32	4.9	104(M)	-
	H_2	1378	35	5.1	78	N.O.
	H_2	(201 KSI)			107(M)	-
Fe-25Mn C.W.30%	Air	1219	14	2.3	106(M)	-
	H_2	1233	13	1.8	86	N.O.
	H_2	(178 KSI)			95	N.O.
	H_2				102(M)	-
Co Alloy C.W.60%	Air	1677	13	1.9	89(M)	-
	H_2	1646	13	2.2	68	N.O.
	H_2	(241 KSI)			79	N.O.
	H_2				84(M)	-
Co Alloy C.W.60% +H.T.	Air	2115	7.5	1.2	82(M)	-
	H_2	2142	6.7	1.0	63	N.O.
	H_2	(309 KSI)			72	N.O.
	H_2				80(M)	-

Notes: (1) H.T. = heat treatment of cobalt alloy - 925°F for 3 1/2 hours

(2) $K_I(M)$ = maximum K_I calculated from load at fracture

(3) N.O. = none observed

(4) Strain rate for tensile tests = $5 \times 10^{-4} \frac{m}{m}$

(5) Elongations are for a one inch gauge length

Single edge notch (SEN) specimens, for which a stress intensity calibration is available (17), and tensile specimens were used to determine the fracture behavior of the alloys. All the SEN specimens were precracked by fatigue loading prior to loading in tension, with the specimens which were tested in hydrogen being precracked in this environment just prior to tensile testing. The tests were run in a hydrogen environment at 91 kNm^{-2} (0.9 atm) and at ambient temperature.

X-ray analysis was carried out using a diffractometer with MoK_{α} radiation.

RESULTS

The mechanical properties data for the alloys in the respective environments are presented in Table II. From the stress intensity

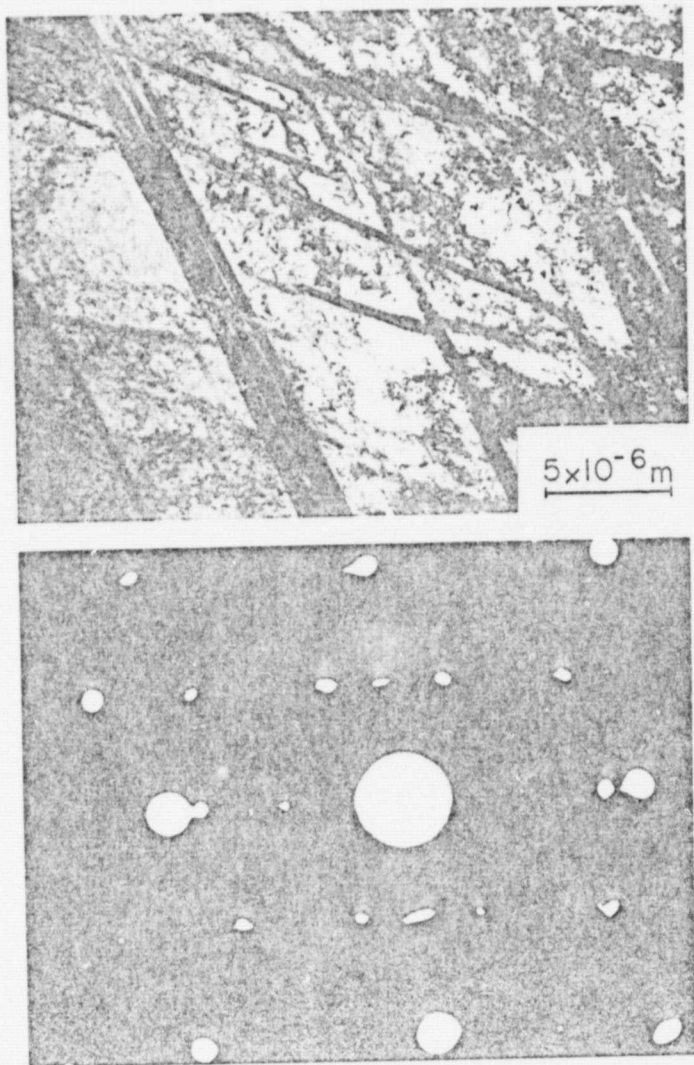


Fig. 1. Two deformation twin variants in an Fe-16Mn alloy deformed 50%.
 (a) Bright field electron micrograph
 (b) Selected area diffraction pattern - the pattern consists of three superimposed reciprocal lattice sections $[125]_{\gamma}$, $[121]_{\text{T}}$ twin I, $[110]_{\text{T}}$ twin II.

values, crack growth rates, and ductility data listed in Table II, it appears that the mechanical properties of none of the alloys were degraded by a hydrogen environment under the test conditions employed. For each alloy in a given metallurgical state scanning electron microscopy observations of the tensile zones on the fracture surfaces revealed essentially the same fracture mode in both the air and hydrogen environments. Magnetic analysis of the iron base alloys in the as received cold worked state and in regions adjacent to fracture surfaces of tensile specimens indicated less than 1% of a magnetic phase in all states with no apparent increase in the Fe-16Mn alloy and with a slight apparent increase in the Fe-25Mn alloy.

For each alloy the initial microstructure in each metallurgical state was determined using primarily transmission electron microscopy techniques in conjunction with x-ray analysis and optical microscopy. Optical microscopy revealed that all of the cold worked alloys exhibited a deformed grain structure with a complex fine deformation structure in the grains. The solution treated Fe-16Mn alloy was fcc. X-ray and transmission electron microscopy techniques were used to examine specimens of this alloy which were cold rolled twenty and fifty percent respectively. X-ray analysis with a diffractometer did not reveal any evidence of a phase other than fcc. Transmission electron microscopy revealed that fcc mechanical twins were the predominant strain induced structure although some strain induced ϵ' -hcp martensite was observed. A bright field transmission electron micrograph of a typical area in the Fe-16Mn alloy cold worked fifty percent contains two sets of bands, Fig. 1a. Analysis of a selected area diffraction pattern from this region with matrix orientation $[125]_y$, Fig. 1b, revealed the presence of fcc mechanical twins and dark field images showed that each set of bands corresponds to a particular $\{111\}$ fcc mechanical twin variant. Previous work by the author has established that there is a high density of dislocations associated with mechanical twins in cold worked specimens of this alloy which may be mostly twin-matrix interface dislocations(6). The fcc matrix contained a dense irregular arrangement of dislocations, Fig. 1a.

X-ray analysis of the Fe-25Mn alloy revealed only a trace of ϵ and no α in an austenitic matrix for the solution treated alloy and a substantial amount of ϵ' with no α' in the alloy cold worked thirty percent. The structure in the Fe-25Mn alloy cold worked thirty percent is illustrated in the dark field micrograph obtained with the $(002)_y$ beam, Fig. 2a. An analysis of the selected area diffraction pattern from region A, Fig. 2b, combined with dark field analysis revealed a $[110]_y$ matrix orientation with a (111) ϵ' variant and a (111) fcc mechanical twin variant. An analysis of a selected area diffraction pattern from region B with the same matrix orientation and dark field analysis indicated the presence of a second ϵ' variant of the type (111) . Epsilon martensite was the predominant strain induced

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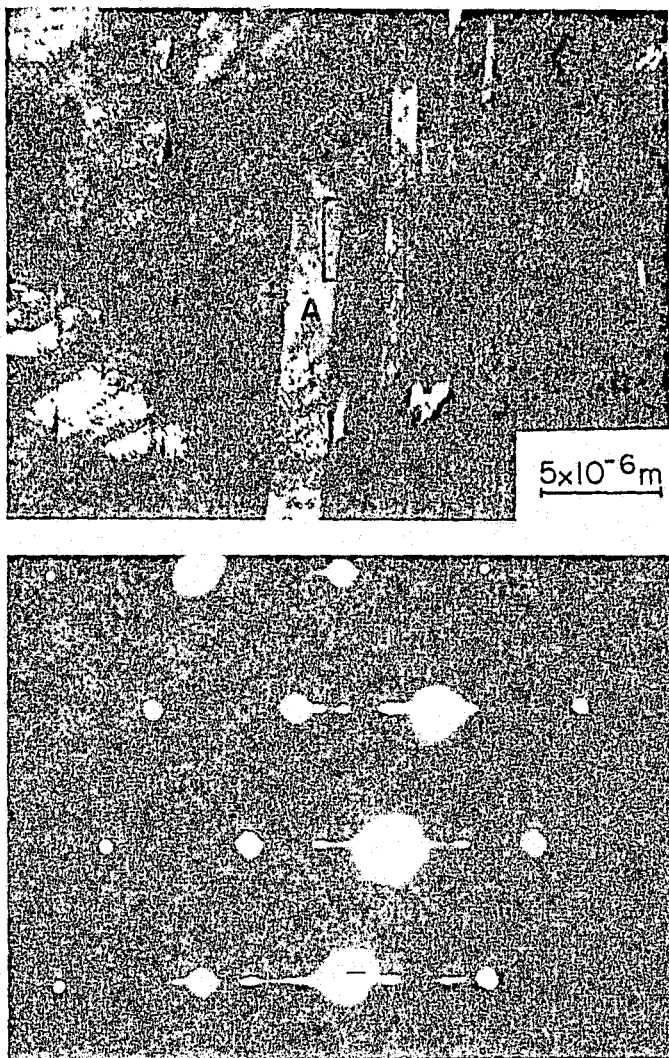


Fig. 2. Typical region in an Fe-25Mn alloy deformed 30%.
 (a) Dark field image with $(002)_{\gamma}$ beam illustrating the band structure
 (b) Selected area diffraction pattern from region A - the pattern consists of three superimposed reciprocal lattice sections $[110]_{\gamma}$, $[1210]_{\epsilon'}$, and $[110]_{\text{T}}$ twin

structure in the Fe-25Mn alloy. A high concentration of defects has been observed to be associated with ϵ' strain induced martensitic bands in heavily cold worked Fe-Mn base alloys (6). The matrix of this alloy also contained a dense irregular arrangement of dislocations, Fig. 2a.

X-ray analysis of the solution treated Co alloy did not indicate the presence of any other phase except the fcc matrix. Transmission electron microscopy revealed occasional widely dispersed carbides and no epsilon martensite. X-ray analysis with a diffractometer of the cold worked alloy did not show evidence for the presence of ϵ' . However, transmission electron microscopy revealed the formation of ϵ' in the cold worked alloy. This type of observation with respect to x-ray analysis with a diffractometer and transmission electron microscopy has been reported previously for some cobalt base fcc alloys in which strain induced ϵ' forms (5). A bright field micrograph of a severely cold worked specimen is illustrated in Fig. 3a. The analysis of the diffraction pattern from this region, Fig. 3b, together with dark field images revealed the presence of two ϵ' variants. A few fcc mechanical twins were also observed in this alloy. The Fe-Mn base and Co-base alloys which were cold worked to high strength levels contain ϵ' -hcp martensite and fcc mechanical twins in an fcc matrix.

The structure present in the cobalt base alloy after severe cold working with subsequent heat treatment is illustrated in the bright field image of Fig. 4a. The phases present were determined from the diffraction pattern of Fig. 4b to be fcc, hcp epsilon, and WC (18). Dark field analysis revealed substantial amounts of epsilon and tungsten carbide. Heat treatment of this alloy has produced a substantial amount of WC and substantial amounts of hcp epsilon have also been retained. Small amounts of $M_{23}C_6$ (18) were sometimes found in some regions of heat treated specimens, but WC is the primary strengthening carbide.

DISCUSSION

High strength cold worked alloys with a broad range of chemistries were resistant to degradation of mechanical properties in a one atmosphere hydrogen environment at ambient temperature. These cold worked alloys were partially strengthened by strain induced ϵ' -hcp martensite and fcc mechanical twins in an fcc matrix. The defect structures associated with the strain induced structures should play a role in strengthening these alloys. Heat treatment of the cobalt alloy after cold working produced a carbide precipitate with retention of an hcp epsilon phase which significantly increased the yield strength level. A TRIP steel with a composition similar to the Fe-25Mn alloy employed in this study which transformed to ϵ' on loading was observed to be resistant to degradation of mechanical properties in a one atmosphere hydrogen environment (16).

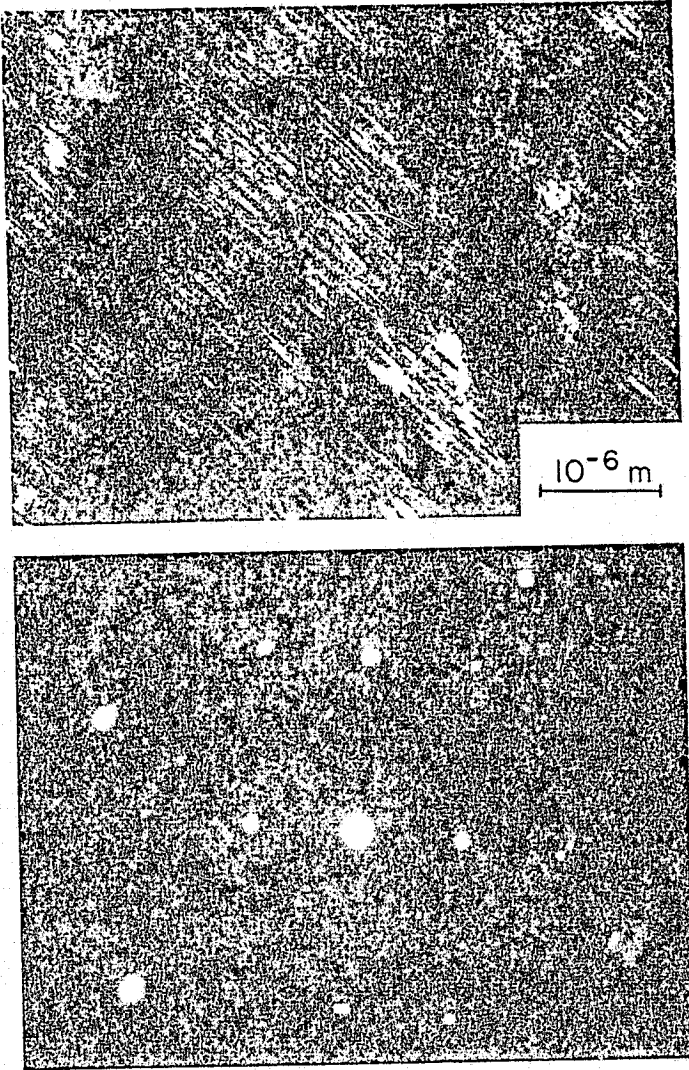


Fig. 3. Typical region in a heavily deformed cobalt alloy.
 (a) Bright field electron micrograph
 (b) Selected area diffraction pattern - the pattern consists of three superimposed reciprocal lattice sections $[121]_{\gamma}$, $[0001]_{\epsilon'}$, and $[1213]_{\epsilon'}$.



Fig. 4. Typical region in the deformed and heat treated cobalt alloy.
(a) Bright field electron micrograph
(b) Selected area diffraction pattern - the pattern reveals three phases: γ -fcc, ϵ -hcp, WC-hex

The ductility of an austenitic steel with a low yield strength in which fcc mechanical twins formed in the matrix and ϵ' formed at the grain boundaries was not reduced in a high pressure hydrogen environment (19).

The decrease in ductility produced by hydrogen in austenitic steels has been observed to be greater the lower the stacking fault energy (SFE) of the alloy for a given set of test conditions with respect to hydrogen (i.e. pressure-temperature of a hydrogen environment or degree of saturation of the alloy with hydrogen)(20,21). Hydrogen appears to be transported with moving dislocations(20,22,23) and it is proposed that the coplanar motion of dislocations in alloys with low SFE will be more effective in nucleating and stabilizing microvoids or microcracks at dislocation barriers(19-23). There is some experimental evidence to support this concept(19,20,22,23). Since the alloys of this investigation which transform to ϵ' and fcc mechanical twins have low stacking fault energies they should be more susceptible in the solution treated low strength state to reduction in ductility by hydrogen than alloys with high stacking fault energies. It has been observed that the ductility of the Fe-16Mn base alloy is decreased somewhat in a $687 \times 10^2 \text{ kNm}^{-2}$ (10^4 PSI) hydrogen environment, although the yield strength and ultimate strength were not decreased(20). It has been shown that high energy rate forging (HERF) which produces dislocation tangles can considerably decrease the ductility losses caused by hydrogen in some alloys(20,21,24). This has been interpreted in some cases in terms of the dislocation tangles tending to force a change in the dislocation structure from coplanar to a more random motion when these alloys are plastically deformed(20,21). The microstructures of the cold worked low SFE alloys of this study are different from those produced by HERF in that there are thin bands of the strain induced structures relatively close together with a dense irregular arrangement of dislocations in the fcc matrix. This type of microstructure could also possibly inhibit coplanar dislocation motion, formation of pileups, and transport of hydrogen (22).

If substantial amounts of stress or strain induced α' -bcc martensite form in an iron base fcc alloy during mechanical testing, it has been observed that a hydrogen environment can degrade the mechanical properties of the alloy(13-16). This has been interpreted in terms of an interaction of hydrogen at the α' (14-16) or at martensitic regions containing $\alpha'+\epsilon'$ (13) being responsible for this degradation. However, it has been proposed recently that the low SFE of some of the alloys in which α' forms is responsible for the degradation of mechanical properties(21,22). Since both the low SFE and the presence of α' might have an effect on a ductility decrease produced by hydrogen in systems where substantial amounts of α' forms during mechanical testing, it appears that further work will be necessary to clarify this matter.

In order to more fully evaluate the role of metallurgical microstructure for the alloys of this investigation, it will be necessary to investigate the effect of more severe conditions with respect to hydrogen on the mechanical properties of the alloys in different metallurgical states. Thermodynamic and kinetic factors can also play an important role in hydrogen environment embrittlement. Several recent papers have discussed in detail the various processes involved in the transport of hydrogen from a molecular gaseous environment to some interior point in a metal, and have stressed that these processes may control whether a hydrogen environment affects the mechanical properties of an alloy under a particular set of test conditions(1,20,22,23,25). These processes consist of several reactions at the gas-metal interface(1,22,25), transport of hydrogen with mobile dislocations(20,22,23), and any reactions that may occur in the metal(1,22,23,25). Temperature and pressure can, of course, have a strong effect on the rates of these processes.

If an fcc alloy which is initially partially strengthened by the formation of strain induced ϵ' martensite and/or fcc mechanical twins during cold working can be further strengthened by a precipitate formed during subsequent heat treatment, then the type and location of the precipitate might play a critical role with regard to the effect of a hydrogen environment on the mechanical properties of the alloy. Carbides and hcp epsilon were the only phases observed in the cobalt alloy of this study after heat treatment. A recent investigation of a nickel base alloy has revealed that the formation of a grain boundary precipitate of $Ni_3(AlTi)$ or impurities segregating to the grain boundary during heat treatment resulted in severe degradation of the mechanical properties of the alloy in a one atmosphere hydrogen environment (26). At ambient temperature many cobalt and iron base alloys contain carbide and intermetallic compound precipitates.

High strength iron and cobalt base alloys with yield strengths in the range of 1233 to 2129 MNm^{-2} (179 to 309 KSI) were resistant to degradation of mechanical properties in a one atmosphere hydrogen environment at ambient temperature under the test conditions employed. The initial high strength levels were produced by cold working the alloys which resulted in the formation of strain induced ϵ' -hcp martensite and fcc mechanical twins in an fcc matrix. Subsequent heat treatment of the cobalt base alloy after cold working produced carbide precipitation with retention of hcp epsilon which resulted in a maximum yield strength level of 2129 MNm^{-2} (309 KSI). For the Fe-25Mn and Co-base alloys the metallurgical microstructure was held approximately constant and the alloy chemistry was varied. For the Co-base alloy the chemistry was held constant and the metallurgical microstructure was varied. This investigation has established that it is possible to produce high strength alloys with certain known microstructures which appear to be resistant to degradation of mechanical properties by a hydrogen environment under certain conditions.

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REFERENCES

1. D. P. Williams and H. G. Nelson: *Met. Trans.*, 1970, vol. 1, pp. 63-68.
2. I. M. Bernstein: *Mater. Sci. Eng.*, 1970, vol. 6, pp. 1-19.
3. R. P. Jewett, R. J. Walter, W. T. Chandler, R. P. Frohberg: NASA Technology Survey, NASA CR-2163, Rocketdyne, Conoga Park, California, March 1973.
4. R. J. Magone, D. B. Roach and A. M. Hall: DMIC Report 113, Battelle Memorial Institute, Columbus, Ohio, May 1959.
5. A. H. Graham and J. L. Youngblood: *Met. Trans.*, 1970, vol. 1, pp. 423-30.
6. R. B. Benson, Jr., D. K. Kim, D. Atteridge, and W. W. Gerberich: to be published in *Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys*, Unieux-Firminy, France, June 1973.
7. J. F. Breedis and L. Kaufman: *Met. Trans.*, 1971, vol. 2, pp. 2359-2371.
8. C. H. White and R. W. K. Honeycombe: *JISI*, 1962, vol. 200, pp. 457-466.
9. K. S. Raghavan, A. S. Sastri and M. J. Marcinkowski: *Trans. Met. Soc. AIME*, 1969, vol. 245, pp. 1569-75.
10. A. Holden, J. D. Bolton and E. R. Petty: *JISI*, 1971, vol. 209, pp. 721-28.
11. J. M. Drapier, P. Viatour, D. Contsouradis and L. Habraken: *Cobalt*, 1970, No. 49, pp. 171-186.
12. Data Sheets on Havar Alloy, Hamilton Precision Metals, Lancaster, Pa.

13. R. B. Benson, Jr., R. K. Dann and L. W. Roberts, Jr.: Trans. Met. Soc. AIME, 1968, vol. 242, pp. 2199-2205.
14. R. A. McCoy and W. W. Gerberich: Met. Trans., 1973, vol. 4, pp. 539-47.
15. R. R. Vandervoort, A. W. Ruotola and E. L. Raymond: Met. Trans., 1973, vol. 4, pp. 1175-78.
16. R. A. McCoy: this conference.
17. W. F. Brown, Jr. and J. E. Srawley: Plane Strain Crack Toughness Testing of High Strength Metallic Materials, ASTM Special Technical Publication 410, p. 12, 1966.
18. H. J. Goldschmidt: Metallurgia, 1947, vol. 40, pp. 103-04.
19. A. W. Thompson: to be published in Mat. Sci. Eng.
20. M. R. Louthan, Jr., G. R. Caskey, Jr., J. A. Donovan and D. E. Rawl, Jr.: Mater. Sci. Eng., 1972, vol. 10, pp. 357-368.
21. A. W. Thompson: this conference.
22. A. W. Thompson: to be published in Met. Trans.
23. M. R. Louthan, Jr.: this conference.
24. M. R. Louthan, Jr., J. A. Donovan and D. E. Rawl, Jr.: Corrosion, 1973, vol. 29, pp. 108-111.
25. H. G. Nelson, D. P. Williams and A. S. Tetelman: Met. Trans., 1971, vol. 2, pp. 953-59.
26. D. P. Williams, R. B. Benson, Jr. and G. Y. Lai: to be published.