Technical Reference on Hydrogen Compatibility of Materials

Carbon and Alloy Steels: 9Ni-4Co (code 1401)

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This document was prepared with financial support from the Safety, Codes and Standards program element of the Hydrogen, Fuel Cells and Infrastructure program, Office of Energy Efficiency and Renewable Energy; Pat Davis is the manager of this program element. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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1. General

9Ni-4Co is a high strength, tempered martensitic steel used primarily in the aerospace industry [1, 2]. Screening tests indicate that this alloy is not appropriate for use in gaseous hydrogen environments [3-5]. Fatigue data indicate that gaseous additives can reduce the embrittling effects of gaseous hydrogen on 9Ni-4Co [6]; however, further study is required to determine the viability and practicality of such an approach.

1.1 Composition

Table 1.1.1 lists the compositional range for 9Ni-4Co steel.

1.2 Other Designations

HP9-4-20, UNS K91472; similar alloys: HP9-4-30 (UNS K91283), HP9-4-25 (UNS91122)

2. Permeability and Solubility

Permeability of hydrogen in 9Ni-4Co is reported to be similar to pure iron and 4130 steel [7, 8]. The temperature dependence of permeability is reported in Ref. [7] as

$$\phi = \phi_o \exp\left(-E_\phi / RT\right)$$

where $\phi_o = 1.95 \times 10^{-4} \frac{\text{mol H}_2}{\text{m} \cdot \text{s} \cdot \sqrt{\text{MPa}}}$ and $E_{\phi} = 39.3 \text{kJ/mol}$.

3. Mechanical Properties: Effects of Gaseous Hydrogen

3.1 Tensile properties

3.1.1 Smooth tensile properties

Walter, Chandler and co-workers [3-5] have categorized 9Ni-4Co steel as extremely embrittled in the presence of hydrogen gas at room temperature. Tensile properties are given in Table 3.1.1.1.

3.1.2. Notched tensile properties

Notched tensile properties of 9Ni-4Co in 69 MPa gaseous hydrogen, Table 3.1.2.1, show that this steel has almost no ductility (RA = 0.2%), and its sharp-notch strength is reduced by a factor of four compared to testing in 69 MPa gaseous helium.

3.2 Fracture mechanics

No known published data in gaseous hydrogen.

3.3 Fatigue

Fatigue crack growth rates were found to be significantly greater in 0.013 MPa gaseous hydrogen compared to vacuum (10^{-6} Pa); measurements are reported at temperatures between 225 and 375 K and cyclic stress intensity in the range of 10 to 50 MPa m^{1/2} [6]. The fatigue crack growth rate in this low pressure of hydrogen is a maximum at about 273K and shows the largest

January 4, 2005

difference compared to vacuum at stress intensity near 25 MPa m^{1/2}. At room temperature and a stress intensity of 24.7 MPa m^{1/2} the fatigue crack growth rate is about 5×10^{-6} m/cycle in hydrogen and 8×10^{-8} m/cycle in vacuum. Equal partial pressures (0.013 MPa) of oxygen (O₂), carbon monoxide (CO) or nitrous oxide (N₂O) added to gaseous hydrogen reduced the fatigue crack growth rates to values associated with those gases alone, about twice the rate in vacuum [6].

3.4 Creep

No known published data in gaseous hydrogen.

4. Fabrication

Special considerations for hydrogen service have not been identified since this alloy is not recommended for hydrogen service.

5. References

- 1. A Magnee, JM Drapier, J Dumont, D Coutsouradis and L Habraken. Cobalt-Containing High-Strength Steels. Centre d'Information du Cobalt, Brussels (1974).
- JL Shannon. Ultra High Strength Steels: Fe-9Ni-4Co-Cr-Mo-V (code 1221). in: WF Brown, H Mindlin and CY Ho, editors. Aerospace Structural Metals Handbook. West Lafayette: CINDAS/UASF CRDA Handbooks Operation, Purdue University (1987).
- 3. RJ Walter and WT Chandler. Effects of High-Pressure Hydrogen on Metals at Ambient Temperature: Final Report (NASA CR-102425). Rocketdyne (report no. R-7780-1) for the National Aeronautics and Space Administration, Canoga Park CA (February 1969).
- 4. RJ Walter, RP Jewitt and WT Chandler. On the Mechanism of Hydrogen-Environment Embrittlement of Iron- and Nickel-base Alloys. Mater Sci Eng 5 (1970) 99-110.
- RP Jewitt, RJ Walter, WT Chandler and RP Frohmberg. Hydrogen Environment Embrittlement of Metals (NASA CR-2163). Rocketdyne for the National Aeronautics and Space Administration, Canoga Park CA (March 1973).
- 6. JD Frandsen and HL Marcus. Environmentally Assisted Fatigue Crack Propagation in Steel. Metall Trans 8A (1977) 265-272.
- MR Louthan, RG Derrick, JA Donovan and GR Caskey. Hydrogen Transport in Iron and Steel. in: AW Thompson and IM Bernstein, editor. Effect of Hydrogen on Behavior of Materials. Metallurgical Society of the AIME (1975) p. 337-347.
- 8. MR Louthan and G Caskey. Hydrogen Transport and Embrittlement in Structural Metals. International Journal of Hydrogen Energy 1 (1976) 291-305.

January 4, 2005

9. ASTM. Metals and Alloys in the UNIFIED NUMBERING SYSTEM (SAE HS-1086 OCT01; ASTM DS-56H). Society of Automotive Engineers; American Society for Testing and Materials, (2001).

Heat	Fe	Ni	Co	Cr	Mn	Mo	Si	С		Ref.
UNS K91472	Bal	8.50 9.50	4.25 4.75	0.65 0.85	0.20 0.40	0.90 1.10	0.20 max	0.17 0.23	0.010 max S; 0.010 max P; 0.35 max Cu; 0.06 < V < 0.12	[9]
W69	Bal	9.10	4.45	0.78	0.27	1.01	0.02	0.17	0.005 P; 0.005 S; 0.78 V	[3]

Table 1.1.1. Compositional ranges of 9Ni-4Co according to UNS K91472.

Table 3.1.1.1. Tensile properties of 9Ni-4Co steel tested at room temperature in high-pressure helium and hydrogen gas.

Material	Thermal precharging	Test environment	Strain rate (s ⁻¹)	S _y (MPa)	S _u (MPa)	El _u (%)	El, (%)	RA (%)	Ref.
W69†	None	69MPa He	0.67	1289	1372		15	67	[2 5]
	None	69MPa H ₂	x10 ⁻³		1207		0.5	15	[3, 5]

† annealed at 843°C (1550°F) for 1 hour, oil quenched; double tempered at 538°C (1000°F) for 2 hours

Table 3.1.2.1. Notched tensile properties of 9Ni-4Co steel tested in high-pressure helium and hydrogen gas at room temperature.

Material	Specimen	Thermal precharging	Test environment	S _y * (MPa)	σ _s (MPa)	RA (%)	Ref.
W69†	(1)	None	69MPa He	1289	2668	6.3	[2 5]
		None	$69 MPa H_2$		614	0.2	[3, 3]

[†] annealed at 843°C (1550°F) for 1 hour, oil quenched; double tempered at 538°C (1000°F) for 2 hours

* yield strength (0.2% offset) of smooth tensile bar

(1) stress concentration factor (K_t) = 8.4; notch geometry = 60° included angle; minimum diameter = 3.81 mm (0.15 inch); maximum diameter = 7.77 mm (0.306 inch); notch root radius = 0.024 mm (0.00095 inch); displacement rate $\approx 4 \times 10^{-4}$ mm/s.