Technical Reference on Hydrogen Compatibility of Materials

Copper Alloys:
Pure Copper (code 4001)

Prepared by:
C. San Marchi, Sandia National Laboratories

Editors
C. San Marchi
B.P. Somerday
Sandia National Laboratories

This report may be updated and revised periodically in response to the needs of the technical community; up-to-date versions can be requested from the editors at the address given below or downloaded at http://www.ca.sandia.gov/matlsTechRef/ . The success of this reference depends upon feedback from the technical community; please forward your comments, suggestions, criticisms and relevant public-domain data to:

Sandia National Laboratories
Matls Tech Ref
C. San Marchi (MS-9402)
7011 East Ave
Livermore CA 94550.

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.

1. General

Nominally pure oxide-free coppers appear to be relatively unaffected by high-pressure hydrogen gas. However, mechanical testing of hydrogen-saturated copper has not been carefully investigated and it is unclear whether long-time exposure to high-pressure hydrogen gas will result in degradation of mechanical properties. The effect of high-pressure hydrogen gas on metals has been quantified in the literature by saturating metals with hydrogen at elevated temperature in high-pressure hydrogen gas [1], a process called thermal precharging. Thermal precharging of copper, however, must be considered carefully. Copper anneals at low temperatures compared to steels, and the permeability of hydrogen in copper is less than most steels; therefore, precharging conditions appropriate for steels may not be appropriate for copper. The diffusivity and solubility of hydrogen in copper is very low, thus equilibrium hydrogen saturation in copper takes exceptionally long times as in stainless steels.

Copper with oxygen inclusions is embrittled by hydrogen [2-4]. Hydrogen reduces copper oxide forming water but can also react with oxygen in solution. In particular, oxides at grain boundaries are believed to promote intergranular failure and loss of ductility. The process of hydrogen embrittlement is slow at ambient temperatures as it requires diffusion of the active species, namely oxygen and hydrogen [2-4].

The available data combined with the observation that pure coppers are relatively low strength seem to indicate that copper is not strongly affected by hydrogen, provided that the copper is oxide-free.

1.1 Composition

There are many varieties of copper, each with compositional requirements designed to meet specific applications. OFHC copper (oxygen-free high-conductivity) is generically employed when oxygen inclusions cannot be tolerated. Hydrogen effects on alloys containing other trace elements, such as phosphorus, have not been reported in the literature with respect to gaseous hydrogen service.

2. Permeability, Diffusivity and Solubility

The permeability of hydrogen through copper (Figure 2.1) is very low, even lower than austenitic stainless steel. The low permeability is due to the combination of low diffusivity for hydrogen (Figure 2.2) and low solubility of hydrogen (Figure 2.3); permeability is the product of solubility and diffusivity. The diffusivity of hydrogen in copper, however, is not as low as in austenitic stainless steels. Table 2.1 summarizes the information plotted in Figures 2.1, 2.2 and 2.3.

3. Mechanical Properties: Effects of Gaseous Hydrogen

3.1 Tensile properties

3.1.1 Smooth tensile properties

The data for OFHC copper is not entirely consistent. Walter and Chandler report essentially no effect of hydrogen on cold drawn OFHC copper (Table 3.1.1.1) [5], while Vennett and Ansell report as much as 16% loss in ultimate strength in material tested in 69 MPa hydrogen gas at constant crosshead displacement of 8.5 x 10^{-3} mm/s (0.02 in/min) [6]. In the latter report, the fracture surface was observed to be along a plane at 45 degrees from the loading axis in 69 MPa hydrogen compared to the double cup fracture observed when tested in air. In addition, Vennett and Ansell observed inclusions in the OFHC copper used in their study [6], perhaps indicating that these hydrogen effects could be attributed to oxides or other second phase inclusions.

Louthan et al. report the same mechanical properties (Table 3.1.1.1) for Cu with internal hydrogen [7] as for OFHC Cu tested in external hydrogen [1]; although this is presumably an error, the properties were unchanged by internal or external hydrogen. In the latter study, significant reductions in strength were reported for boron deoxidized copper with internal hydrogen [1]. These strength reductions, however, were accompanied by slight improvements in ductility, which implies that these reductions may have been due to annealing at the precharging temperature. Louthan also reports a reduction in strength for the boron-deoxidized copper when tested in high-pressure hydrogen gas; the source of this degradation is unclear, but remains suspect considering the ambiguities associated with data from Louthan et al.

3.1.2. Notched tensile properties

Notched tensile properties show the same trends as smooth tensile properties. High-pressure gaseous hydrogen is reported to have no effect on notched tensile properties of OFHC copper (Table 3.1.2.1) [5]; at least for copper that showed no degradation in properties in smooth-bar tensile tests. Details of notched tensile properties are not reported for a different heat of OFHC copper used by Vennett and Ansell, however, a loss of ultimate strength was observed in notched-bar tensile tests as in smooth-bar tensile tests (tested in high-pressure hydrogen gas) [6].

3.2 Fracture mechanics

No known published data in hydrogen gas.

3.3 Fatigue

No known published data in hydrogen gas.

3.4 Creep

No known published data in hydrogen gas.

3.5 Impact

No known published data in hydrogen gas.

3.6 Disk rupture tests
Hydrogen is reported to have no effect on copper in disk rupture tests [8]. There are no reports of extended hydrogen exposures prior to disk rupture tests.

4. Metallurgical considerations
Despite the paucity of data for nominally pure coppers in the presence of high-pressure hydrogen gas, it appears that oxide inclusions are the most detrimental features for resistance to hydrogen-assisted fracture. The presence of oxide inclusions may explain the change in fracture morphology observed in tensile testing of copper in high-pressure air compared to high-pressure hydrogen gas [6].

5. References

1. MR Louthan and G Caskey. Hydrogen Transport and Embrittlement in Structural Metals. Int J Hydrogen Energy 1 (1976) 291-305.
2. E Mattsson and F Schueckher. An investigation of hydrogen embrittlement in copper. Journal of the Institute of Metals 87 (1958-59) 241-247.
3. GR Caskey, AH Dexter, ML Holzworth, MR Louthan and RG Derrick. Hydrogen Transport in Copper (DP-MS-75-6). Savannah River Laboratory, Aiken SC (1975).
4. GR Caskey, AH Dexter, ML Holzworth, MR Louthan and RG Derrick. The Effect of Oxygen on Hydrogen Transport in Copper. Corrosion 32 (1976) 370-374.
5. 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).
6. RM Vennett and GS Ansell. A Study of Gaseous Hydrogen Damage in Certain FCC Metals. Trans ASM 62 (1969) 1007-1013.
7. MR Louthan, GR Caskey, JA Donovan and DE Rawl. Hydrogen Embrittlement of Metals. Mater Sci Eng 10 (1972) 357-368.
8. J-P Fidelle, R Bernardi, R Broudeur, C Roux and M Rapin. Disk Pressure Testing of Hydrogen Environment Embrittlement. in: Hydrogen Embrittlement Testing, ASTM STP 543, American Society for Testing and Materials. (1974) p. 221-253.
9. DW Rudd, DW Vose and S Johnson. Permability of Copper to Hydrogen. J Phys Chem 65 (1961) 1018-1020.
10. JK Gorman and WR Nardella. Hydrogen Permeation through Metals. Vacuum 12 (1962) 19-24.
11. W Eichenauer, W Loser and H Witte. Solubility and rate of diffusion of hydrogen and deuterium in nickel and copper single crystals. Z Metallk 56 (1965) 287-293.
12. L Katz, M Guinan and RJ Borg. Diffusion of H_2, D_2, and T_2 in Single-Crystal Ni and Cu. Phys Rev B 4 (1971) 330-341.
13. DR Begeal. Hydorgen and deuterium permeation in copper alloys, copper-gold brazing alloys, gold, and the in situ growth of stable oxide permeation barriers. J Vac Sci Technol 15 (1978) 1146-1154.
14. T Tanabe, Y Tamanishi, K Sawada and S Imoto. Hydrogen Transport in Stainless Steels. J Nucl Mater 122&123 (1984) 1568-1572.

15. 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).

Table 2.1. Permeability, diffusivity and solubility relationships for copper.

Material	Temperature Range (K)	Pressure Range (MPa)	$\Phi = \Phi_o \exp(-E_\Phi / RT)$		$D = D_o \exp(-E_D / RT)$		$S = S_o \exp(-E_S / RT)$		Ref.
			Φ_o $\left(\frac{\text{mol H}_2}{\text{m} \cdot \text{s} \cdot \text{MPa}^{1/2}}\right)$	E_Φ $\left(\frac{\text{kJ}}{\text{mol}}\right)$	D_o $\left(\frac{\text{m}^2}{\text{s}}\right)$	E_D $\left(\frac{\text{kJ}}{\text{mol}}\right)$	S_o $\left(\frac{\text{mol H}_2}{\text{m}^3 \cdot \text{MPa}^{1/2}}\right)$	E_S $\left(\frac{\text{kJ}}{\text{mol}}\right)$	
Pure Cu	623–773	0.15–0.2	263 x 10^{-4}	52.3	—	—	—	—	[9]
OFHC Cu	623–973	0.1	4.46 x 10^{-4}	75.3	—	—	—	—	[10]
Single crystal Cu	700–925	0.013–0.093	5.26 x 10^{-4}	78.7	11.5 x 10^{-6}	40.8	458	37.9	[11]
			3.31 x 10^{-4} (D)	77.8 (D)	6.2 x 10^{-6} (D)	37.8 (D)	534 (D)	40.0 (D)	
Single crystal Cu	723–1198	—	—	—	11.3 x 10^{-6}	38.9	—	—	[12]
			—	—	7.30 x 10^{-6} (D)	36.8 (D)	—	—	
			—	—	6.12 x 10^{-6} (T)	36.5 (T)	—	—	
Several low oxygen coppers †	350–750	0.1–0.5	0.821 x 10^{-4}	71.7	8.6 x 10^{-6}	52.4	9.5	19.3	[3, 4]
OFHC Cu	493–713	0.0013–0.13	8.40 x 10^{-4}	77.4	1.06 x 10^{-6}	38.5	792	38.9	[13]
Cu	500–1200	0.001–0.1	0.366 x 10^{-4}	60.5	0.226 x 10^{-6}	29.3	162	31.2	[14]

(D) and (T) denote values as measured for deuterium and tritium respectively.

† Data from Refs. [3, 4] are determined for deuterium: permeability and diffusivity have been corrected here to give permeability and diffusivity of hydrogen (by multiplying by the square root of the mass ratio: $\sqrt{2}$); solubility is assumed to be independent of isotope. Diffusivity is estimated from Figure 6 in Refs. [3, 4]; solubility is calculated $(S = \Phi / D)$.

Table 3.1.1.1. Smooth tensile properties of copper at room temperature: measured in external hydrogen gas.

Material	Thermal precharging	Test environment	Strain rate (s^{-1})	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)	Ref.
Cold drawn, OFHC Cu	None	69 MPa He	—	269	290	—	20	94	[5, 15]
	None	69 MPa H_2		—	283	—	20	94	
Cu	None	Air	—	96	234	—	44	71	[7]
	(1)	Air		96	228	—	45	71	
OFHC Cu	None	Air	—	96.5	234	—	44	71	[1]
	None	69 MPa H_2		96.5	228	—	45	71	
Boron deoxidized Cu	None	Air	—	96.5	234	—	40	92	[1]
	(2)	Air		55.2	200	—	49	92	
	None	69 MPa H_2		68.9	214	—	46	94	
	(2)	69 MPa H_2		41.4	200	—	51	96	

(1) 69 MPa hydrogen, 428 K, 720 h: ~0.03 wppm hydrogen (<1 appm)
(2) 300 MPa hydrogen, 473 K, 1344 h

Table 3.1.2.1. Notch tensile properties of copper at room temperature: measured in external hydrogen gas.

Material	Specimen	Thermal precharging	Test environment	Displ rate (mm/s)	S_y † (MPa)	σ_s (MPa)	RA (%)	Ref.
Cold drawn, OFHC Cu	(a) $K_t \approx 8.4$	None	69MPa He	4×10^{-4}	269	600	20	[5, 15]
		None	69MPa H_2		—	593	24	

K_t = stress concentration factor
† yield strength of smooth tensile specimen
(a) V-notched specimen: 60° included angle; minimum diameter = 3.81 mm; maximum diameter = 7.77 mm; notch root radius = 0.024 mm.

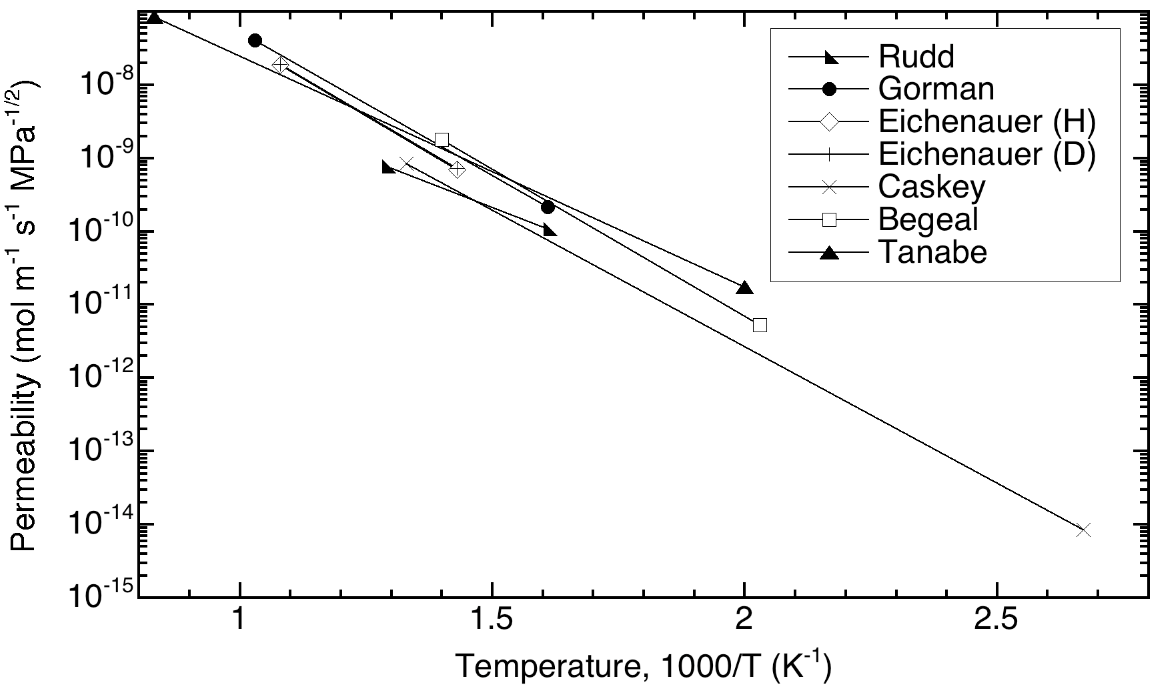

Figure 2.1. Permeability relationships (Table 2.1) for copper: Rudd [9]; Gorman [10]; Eichenauer [11]; Caskey [3, 4]; Begeal [13]; Tanabe [14]. Deuterium (D) data have been corrected to hydrogen (by multiplying by the square root of the mass ratio: √2).

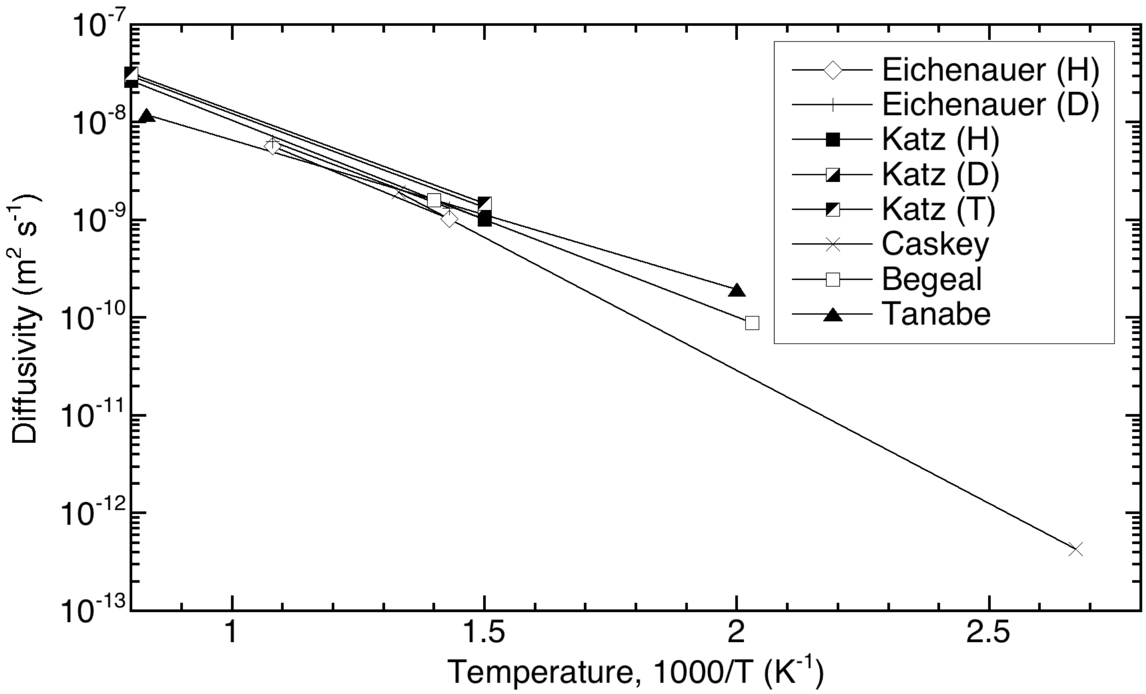

Figure 2.2. Diffusivity relationships (Table 2.1) for copper: Eichenauer [11]; Katz [12]; Caskey [3, 4]; Begeal [13]; Tanabe [14]. Deuterium (D) and tritium (T) data have been corrected to hydrogen (by multiplying by the square root of the mass ratio: √2 and √3 respectively).

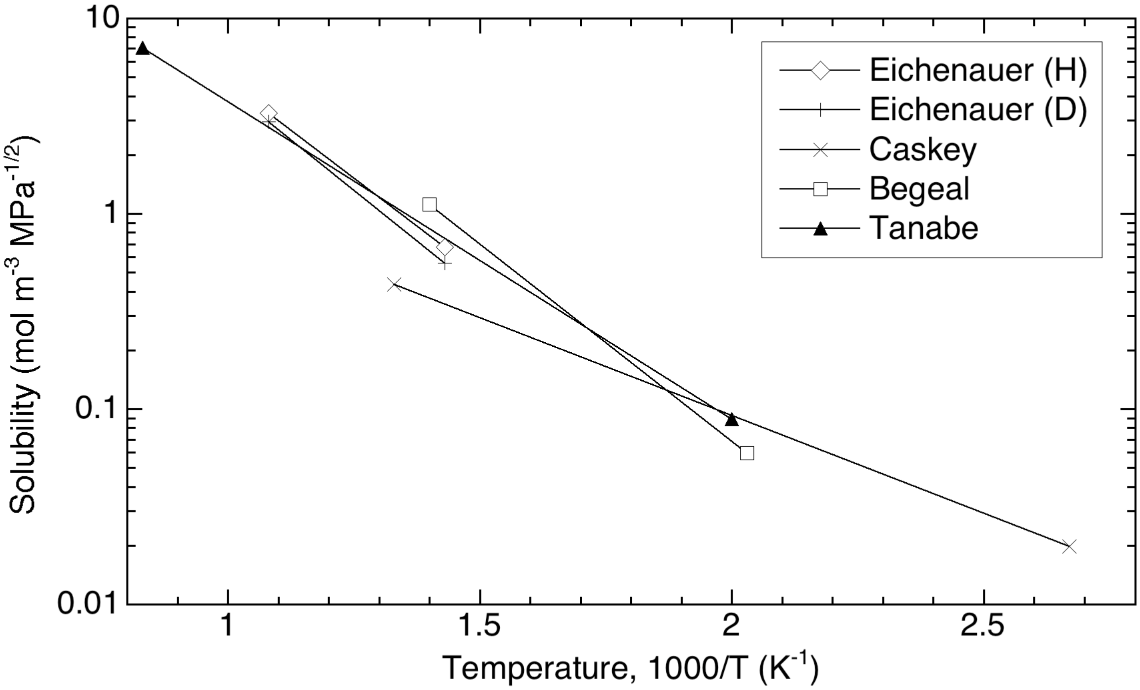

Figure 2.3. Solubility relationships (Table 2.1) for copper: Eichenauer [11]; Caskey [3, 4]; Begeal [13]; Tanabe [14]. Solubility is assumed to be independent of isotope effect, thus solubility of deuterium is nominally the same as for hydrogen.