

Technical Reference on Hydrogen Compatibility of Materials

Specialty Steels: Sealing Alloys Fe-Ni-Co (code 2401)

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1. General

The Fe-Ni-Co alloys under consideration here were developed as metal-ceramic (or metal-glass) seals and designed to match the coefficient of thermal expansion of the ceramic (or glass) phase. Two of the more common alloys have composition of Fe-29Ni-17Co for borosilicate glass and Fe-27Ni-25Co for alumina [1]. These alloys are single-phase austenite with relatively low strength (<700 MPa).

There is very little published information on hydrogen embrittlement for these alloys [1]. The available information shows that in the annealed condition the fracture behavior of Fe-29Ni-17Co is unaffected by high concentrations of internal hydrogen and Fe-27Ni-25Co is unaffected by external high-pressure (69 MPa) hydrogen gas. Limited tensile testing of cold-worked Fe-27Ni-25Co also indicates no susceptibility to hydrogen embrittlement for the higher strength condition.

Permeability of hydrogen in the single-phase Fe-Ni-Co alloys appears to be similar to the austenitic (300-series) stainless steels such as 304 and 316. Diffusivity, however, is higher than other austenitic alloys and solubility somewhat lower.

1.1 Composition

Table 1.1.1 lists nominal compositions for two specialty steels used for making metal-ceramic and metal-glass joints, as well as standard designations and common tradenames.

1.2 Other designations

These alloys have a large number of trade names, which differ from region to region. Table 1.1.1 provides a partial list of the more common designations. In this document the different alloys are referred to by their nominal composition.

2. Permeability and Solubility

There is limited data on permeability, diffusivity and solubility of hydrogen in Fe-Ni-Co specialty sealing alloys. The available data show the permeability to be very similar to austenitic stainless steels such as 304 and 316, Figure 2.1. The apparent diffusivity, however, is a factor of five to ten greater for Fe-29Ni-17Co and Fe-27Ni-25Co than for austenitic stainless steel, Figure 2.2. Thus, the solubility (determined from the ratio of permeability to diffusivity) is a factor of five to ten lower for the Fe-29Ni-17Co and Fe-27Ni-25Co than for the austenitic stainless steels, Figure 2.3. The relationships reported in the Figures 2.1-2.3 are given in Table 2.1 for permeability and diffusivity and in Table 2.2 for solubility. Diffusion measurements tend to have a much greater variation between studies than permeability, possibly due to differences in surface preparation of the permeation membranes. Consequently, due to the limited number of studies, the diffusivity and solubility reported for Fe-29Ni-17Co and Fe-27Ni-25Co should be viewed critically, particularly with regard to the activation energy term.

3. Mechanical Properties: Effects of Gaseous Hydrogen

3.1 Tensile properties

3.1.1 Smooth tensile properties

The tensile properties of Fe-29Ni-17Co and Fe-27Ni-25Co show no significant effect of hydrogen; this statement is based on a single report from the literature [1]. Fe-27Ni-25Co was tested in both the cold-worked and annealed conditions in high-pressure (external) hydrogen gas at 69 MPa. Fe-29Ni-17Co was tested in the annealed condition with internal hydrogen (thermally precharged: 69 MPa hydrogen gas at 430 K for 6500 h). All specimens were tested at an initial strain rate of $1.67 \times 10^{-4} \text{ s}^{-1}$. Gauge diameter was either 2.9 mm or 6.3 mm with a gauge length of 25 mm.

In addition, tubular specimens of Fe-29Ni-17Co were pressurized with 69 MPa hydrogen gas, sealed and heated at 345 K or 430 K for 2900 h or 17500 h. These specimens (9.5 mm outer diameter, 6.4 mm inner diameter) were subsequently tested in tension. The reduction of area of these thermally-precharged, tubular specimens was unchanged compared to specimens tested without exposure to hydrogen [1].

3.1.2. Notched tensile properties

Testing of notched tensile specimens of Fe-29Ni-17Co with internal hydrogen show essentially no change in reduction of area compared to unexposed specimens [1]. Thermal precharging was performed in 69 MPa hydrogen gas at 430 K for 6500 h. The maximum and minimum diameters of the notched tensile specimens were 7.1 and 5.1 mm respectively with a 60° included angle ($K_t \approx 5$). Testing was conducted at a rate of approximately $4 \times 10^{-3} \text{ mm s}^{-1}$.

3.2 Fracture mechanics

3.2.1 Fracture toughness

No known data in hydrogen gas.

3.2.2 Threshold stress intensity factor

No known data in hydrogen gas.

3.3 Fatigue

No known data in hydrogen gas.

3.4 Creep

No known data in hydrogen gas.

3.5 Impact

Internal hydrogen does not significantly affect the notched impact energy of annealed Fe-29Ni-17Co: the impact energy of thermally precharged specimens (69 MPa, 430 K, 6500 h) was 14.1 J compared to 14.3 J for the annealed material not exposed to hydrogen [1]. Impact velocity was 3.4 m/s, and $K_t \approx 5$ (maximum and minimum diameters were 5.7 and 3.8 mm respectively with a 45° notch).

3.6 Disk rupture tests

No known data in hydrogen gas.

4. Metallurgical Considerations**4.1 Primary processing**

Effects of processing on the hydrogen-assisted fracture of these alloys are unknown. As long as the alloy remains single-phase austenite, it is expected that the material will remain resistant to hydrogen embrittlement. Based on data for stable austenitic stainless steel (see other chapters of this resource), it can be expected that increasing strength by warm or cold working will have a negligible to modest effect on hydrogen embrittlement as long as the yield strength remains lower than about 700 MPa (and the alloy remains single-phase).

4.2 Heat treatment

These alloys are typically not heat-treated, which is generally expected to improve resistance to hydrogen-assisted fracture.

4.3 Properties of welds

No known data in hydrogen gas.

5. References

1. AW Thompson and WN Posey. Effect of Hydrogen on Iron-Nickel-Cobalt Sealing Alloys. *J Test Eval* 2 (1974) 240-242.
2. RH Collins and JC Turnbull. Degassing and Permeation of Gases in Tube Materials. *Vacuum* 11 (1961).
3. JK Gorman and WR Nardella. Hydrogen Permeation through Metals. *Vacuum* 12 (1962) 19-24.
4. DJ Mitchell and EM Edge. Permeation characteristics of some iron and nickel based alloys. *J Appl Phys* 57 (1985) 5226-5235.
5. DR Begeal. The permeation and diffusion of hydrogen and deuterium through Rodar, tin-coated Rodar, and solder-coated Rodar. *J Vac Sci Technol* 12 (1975) 405-409.
6. MR Louthan and RG Derrick. Hydrogen Transport in Austenitic Stainless Steel. *Corros Sci* 15 (1975) 565-577.

Table 1.1.1. Nominal composition and common designations for specialty austenitic Fe-Ni-Co sealing alloys.

Nominal composition	UNS designation	Specifications	Common names and Tradenames
Fe-29Ni-17Co	UNS K94610 UNS K 94630	ASTM F-15 ASTM F-1466	Kovar Alloy F15 Nilo K Therlo Lock-Invar Rodar
Fe-27Ni-25Co	UNS K94620	ASTM F-1466	Ceramvar

Table 2.1. Permeability and diffusivity relationships for Fe-Ni-Co alloys.

Material	Temperature Range (K)	Pressure Range (MPa)	$\Phi = \Phi_o \exp(-E_\Phi / RT)$	$D = D_o \exp(-E_D / RT)$	$\frac{\Phi_o}{\text{mol H}_2 \cdot \text{m} \cdot \text{s} \cdot \sqrt{\text{MPa}}}$	$E_\Phi \left(\frac{\text{kJ}}{\text{mol}} \right)$	$D_o \left(\frac{\text{m}^2}{\text{s}} \right)$	$E_D \left(\frac{\text{kJ}}{\text{mol}} \right)$	Ref.
Fe-28Ni-18Co	~373~673	0.1	0.0044×10^{-3}	44.8			---	---	[2]
Fe-29Ni-17Co	773-1223	0.1	0.24×10^{-3}	66.9			---	---	[3]
Fe-29Ni-17Co †	473-673	0.1	9.8×10^{-5}	57.9	3.6×10^{-7}	43.4			[4]
Fe-29Ni-17Co	453-823	0.001-0.1	6.9×10^{-5}	56.5	6.3×10^{-7}	46.4			[5]
Fe-29Ni-17Co †	503-823	0.001-0.1	9.5×10^{-5}	58.2	3.7×10^{-7}	43.1			[5]
Fe-27Ni-25Co †	473-673	0.1	0.13×10^{-3}	57.9	7.2×10^{-7}	45.3			[4]
Fe-27Ni-25Co	453-743	0.001-0.1	0.11×10^{-3}	58.6	6.1×10^{-7}	46.0			[5]

† Measurements made with deuterium: permeability and diffusivity have been corrected here to give permeability of hydrogen (by multiplying by the square root of the mass ratio: $\sqrt{2}$).

Table 2.2. Solubility relationships for Fe-Ni-Co sealing alloys determined from the ratio of permeability and diffusivity (Table 2.1).

Material	Temperature Range (K)	Pressure Range (MPa)	$S = S_o \exp(-E_s/RT)$		Ref.
			S_o $\left(\frac{\text{mol H}_2}{\text{m}^3 \cdot \sqrt{\text{MPa}}} \right)$	E_s $\left(\frac{\text{kJ}}{\text{mol}} \right)$	
Fe-29Ni-17Co †	473-673	0.1	269	14.5	[4]
Fe-29Ni-17Co	453-823	0.001-0.1	109	10.0	[5]
Fe-29Ni-17Co †	503-823	0.001-0.1	259	15.1	[5]
Fe-27Ni-25Co †	473-673	0.1	178	12.5	[4]
Fe-27Ni-25Co	453-743	0.001-0.1	177	12.6	[5]

† Measurements made with deuterium: solubility is assumed to be independent of isotope.

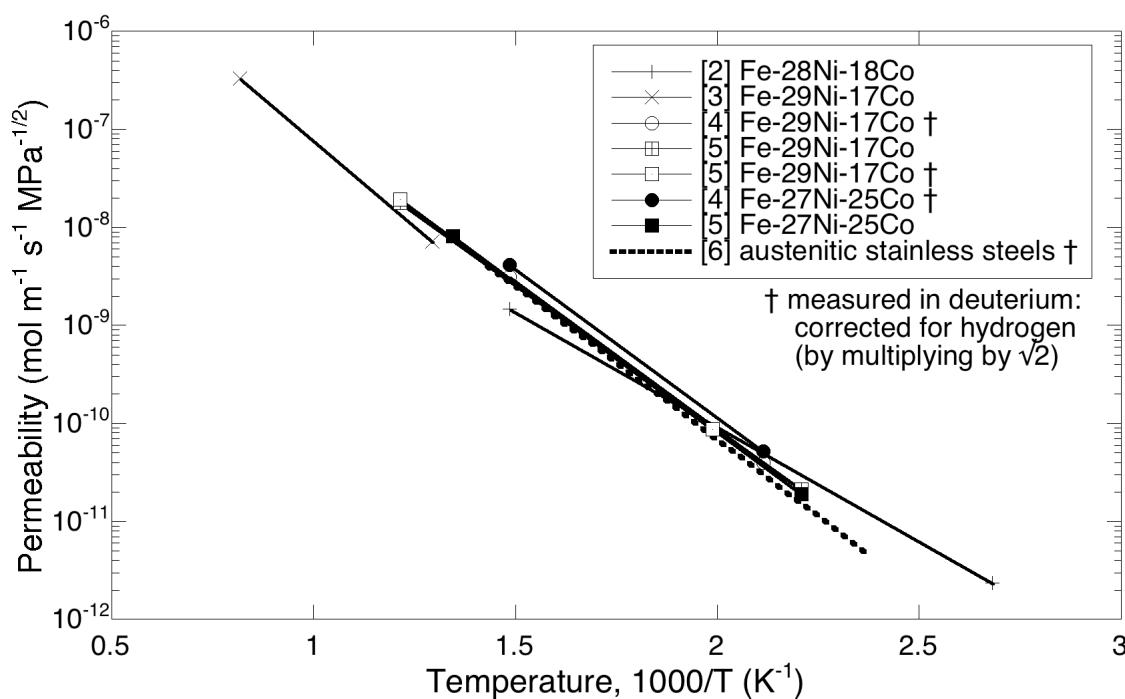


Figure 2.1. Permeability as a function of temperature (Table 2.1) for Fe-Ni-Co sealing alloys. Also plotted (dashed line) relationship for austenitic stainless steels from Ref. [6].

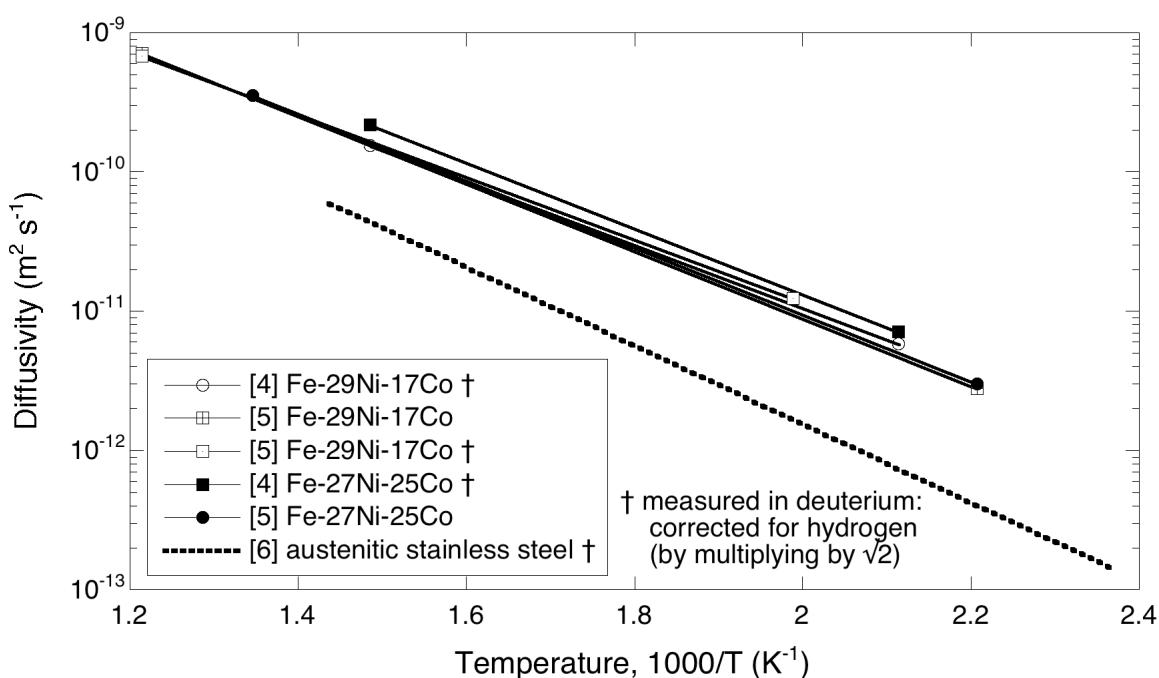


Figure 2.2. Diffusivity as a function of temperature (Table 2.1) for Fe-Ni-Co sealing alloys. Also plotted (dashed line) relationship for austenitic stainless steels from Ref. [6].

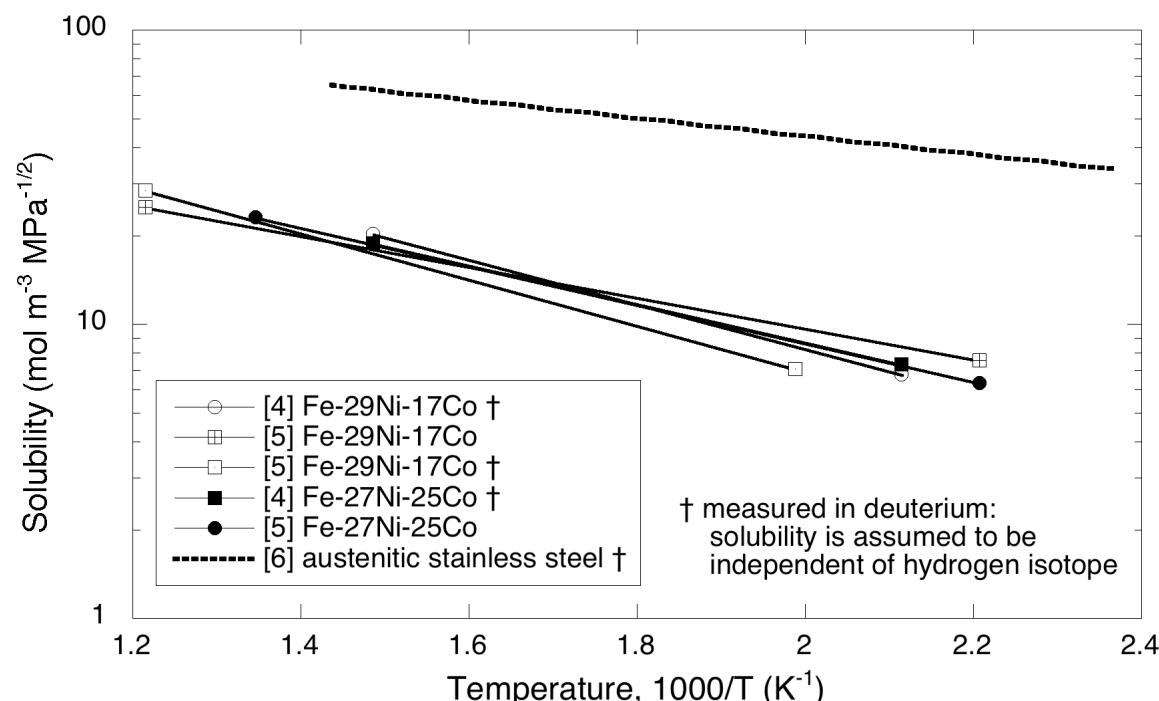


Figure 2.3. Solubility as a function of temperature (ratio of permeability and diffusivity, Table 2.2) for Fe-Ni-Co sealing alloys. Also plotted (dashed line) relationship for austenitic stainless steels from Ref. [6].