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Hydrogen diffusion and trapping in a precipitation-hardened nickel–copper–aluminum alloy Monel K-500 (UNS N05500)

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Abstract

Hydrogen uptake, diffusivity and trap binding energy were determined for the nickel–copper–aluminum alloy Monel K-500 (UNS N05500) in several conditions. The total atomic hydrogen (H) concentration increased from 0 to 132 wppm as the hydrogen overpotential decreased to −0.5 V in alkaline 3.5% NaCl electrolyte at 23 °C. The room-temperature H diffusion coefficient ranged from 0.9 to 3.9×10^{-14} m^2 s^{-1} for single-phase solid solution, aged, and cold worked then aged microstructures. Diffusivity was independent of lattice H concentration but depended weakly on metallurgical condition, with slower H diffusion after aging. The apparent activation energy for H diffusion was in the range of 29–41 ± 1.5 kJ mol^{-1} at the 95% confidence level. The lower value approached nearly perfect lattice transport, while the high value was strongly influenced by traps of low-to-intermediate strength. Atomic hydrogen trapping at metallurgical sites, strongly suggested to be spherical-coherent γ′ (Ni_3Al) precipitates, was evident in the aged compared to the solution heat treated + water-quenched condition. Both thermal desorption and classical Oriani trap state analyses confirmed that the apparent hydrogen trap binding energy interpreted as Ni_3Al (10.2 ± 4.6 kJ mol^{-1}) interfaces was significantly less than the activation energy for perfect lattice diffusion (25.6 ± 0.5 kJ mol^{-1}) in this nickel-based alloy system.

Keywords: Age hardening; Nickel alloy; Hydrogen diffusion and trapping; Hydrogen embrittlement; Hydrogen desorption

1. Introduction

Monel K-500 alloy (UNS N05500) is a precipitation-hardenable nickel–copper (64% Ni–30% Cu–3% Al, wt.%) alloy strengthened by a combination of cold work and age hardening to form fine coherent precipitates [1]. The aged alloy contains spherical, coherent $Ni_3(Al,X)$ and $Ni,Fe_3(Al,Fe)$ phases, with the former known as γ′, where X = Cu, Mn, Ti or Si, present in an Ni–Cu face-centered cubic (fcc) solid solution [2]. The misfit strain is small, which accounts for the spherical shape [3]. Notably, these homogeneously nucleated and uniformly distributed precipitates are absent in alloys solution heat treated (SHT) above 750 °C when thin and rapidly water-quenched (WQ) [2]. This differs from other Ni–Al and Ni–Ti alloys, where γ′ forms readily on quenching [4]. The precipitates can form 6–7% by volume upon aging at 700 °C or less, and remain spherical and coherent during coarsening [2]. Incoherent TiC phases are present in SHT + WQ alloys, but exhibit little shape or size change with aging [2]. $M_{23}C_6$ carbides, where M = Mn, Fe or Ni, form on isolated grain boundaries in Monel K-500 aged for long times. Lastly, annealing twins are prevalent in SHT + WQ, air-cooled or aged material; however, their interface energy is believed to be only a small percentage of the grain boundary energy [2,5]. These metallurgical features are pertinent to H uptake, diffusion and trapping.

Monel K-500 was believed to be relatively immune to hydrogen environment assisted cracking (HEAC) and stress corrosion cracking (SCC) in various natural environments [6]. SCC in H_2S environments under high-stress,

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high-pressure and high-temperature steam, in HF vapors and in Hg was noted for Monel 400 and aged Monel K-500 [7]. Reports also began to indicate susceptibility to room-temperature hydrogen environment embrittlement [8–10], observed as reductions in tensile ductility and notch strength ratio upon cathodic charging. Embrittlement of SHT + aged Monel K-500 (Rockwell C 25-35) occurred in seawater at room temperature when coupled to zinc and where dissolved hydrogen levels increased during prolonged exposure (8 weeks) to 50 wppm. A dynamic plastic strain rate effect was also observed even for pre-charged material [9,11]. Bolt failures have been also observed in age-hardened Monel K-500 subjected to cathodic polarization. Failures by intergranular cracking were attributed to hydrogen embrittlement as a result of cathodic polarization, such as when coupled to aluminum anodes in seawater [7,11]. This was first attributed to high thread root hardness (~HRC 39) due to age hardening after thread machining. Annealing then age hardening was recommended after threading to maintain hardness below a proposed limit (HRC 35) for Monel K-500 in sour systems. However, additional failures have occurred in roll-threaded Monel K-500 bolts annealed at 980–1050 °C, WQ and precipitation-hardened at 500–600 °C for 16 h, producing a Rockwell C hardness of only 25 [11]. This level is below one limit recommended by a US Federal Specification for aged round products [12]. Embrittlement failures also occurred in bolts after about 1 year under a load of about 60% of the tensile yield strength and cathodically protected with anode grade aluminum, even after issuance of modified specifications [7,11]. Intergranular cracking occurred under slow strain rate testing in air after H pre-charging when coupled to Al, or when charged potentiostatically (annealed and SHT + aged Monel K-500), and to a lesser extent when coupled to steel or potentiostatically polarized to −800 mV vs. Ag/AgCl (STA + aged) in ASTM artificial ocean water [13].

The HEAC behavior of Ni-based superalloys stressed in gaseous H_2 and various aqueous exposures has been reviewed in detail elsewhere [14]. The severity of this cracking problem is apparent in many Ni-based alloys, such as Alloy 718 [14]. However, few studies have documented the threshold stress intensity (K_{th}) for HEAC of Monel K-500 and there are no reports on crack growth rate data for controlled testing. In limited work, K_{th} for aged Monel K-500 (R_C 30) decreased from above 70 MPa $\sqrt{m}$ at $-0.7\ V_{SCE}$ to less than 18 MPa $\sqrt{m}$ when stressed in room-temperature NaCl solution at $-1.0\ V_{SCE}$. Crack growth rates were not reported [15]. Moreover, little is known about hydrogen uptake, transport and trapping behavior in this alloy that would contribute to a quantitative understanding and micromechanical model prediction of HEAC [14]. The effective hydrogen diffusion coefficient in pure, single-crystal Ni was reported to be 8.4×10^{-10} $cm^2\ s^{-1}$ at 23 °C, with an activation energy of 39.5 kJ mol^{-1} [16]. Computation using transition state theory indicated that the activation energy reached 45.7 kJ mol^{-1} for a perfect Ni lattice [16]. An Ni–30 at.% Cu alloy had a hydrogen diffusivity of 3×10^{-10} $cm^2\ s^{-1}$ at 23 °C and an activation energy of ~41 kJ mol^{-1} [13]. The effective diffusion coefficient, D_{eff}, which may be H-trap sensitive, was reported to be 5.6×10^{-11} $cm^2\ s^{-1}$ at 23 °C [17] for SHT (950 °C well above the γ' solvus) and radiatively cooled for Monel K-500. The hardness was not reported, and the degree of aging upon cooling was uncertain. Aged alloy X-750 (Ni–Cr–Fe–Al–Ti) shows a drop in effective hydrogen diffusivity of a factor of ~9 from pure Ni, which is attributed to composition differences and H trapping at (Ti,Nb)C particles. An additional decrease by a factor of five in effective diffusivity was attributed to precipitation of γ' Ni_3(Al,Ti) [18]. These results substantiate the importance of H trapping in Ni-based alloys and demonstrate that trapping depends on composition and microstructure.

H-metal–microstructure interactions likely differ between Monel K-500 and high-strength steels because the activation energy for perfect lattice diffusion is low in high-strength steel (i.e. 7 kJ mol^{-1}), while trap binding energies can be as high as 65 kJ mol^{-1} [19]. In contrast, Ni-based fcc lattices have high activation energies. Moreover, possible trapping sites will differ for precipitation-hardened fcc Ni-based alloys compared to ferrous martensitic microstructures. Hydrogen-assisted cracking susceptibility is controlled by crack tip diffusible hydrogen concentration, which is controlled by the hydrogen overpotential and production rate [20]. Metallurgical trap states are important and serve as benign sinks for hydrogen, function as crack tip damage initiation sites and the crack propagation path itself, or function as a reservoir of hydrogen that can be supplied to the tensile triaxial stress field of the stationary or moving crack tip [17,21–23]. Additionally, stage II environmental crack velocities, $[da/dt]_{II}$, at the upper bounds of hydrogen uptake rates, where cracking is not surface uptake limited, are often controlled by the D_{eff} in the zone of material at the crack tip [23]. These parameters likely differ between SHT, cold-worked and aged Monel K-500. The diffusible hydrogen concentration, $C_{H,diff}$, absorbed in the Ni-based alloy as a function of cathodic potential, and D_{eff} for H are critical for understanding and modeling $[da/dt]_{II}$ and K_{th} for Monel K-500. However, $C_{H,diff}$ behavior has not been established as a function of hydrogen overpotential or cathodic hydrogen production rate for Monel K-500. Moreover, D_{eff} and trapping behavior have not been elucidated over a range of technologically significant microstructural conditions, which include cold work and aging time/temperature.

The objective was to characterize $C_{H,diff}$, D_{eff}, and microstructural H trapping behavior in Monel K-500 by comparing SHT/WQ, SHT + artificially aged, SHT + cold worked, as well as SHT + cold-worked + aged variants of this alloy. Experimental data were acquired by the thermal desorption spectroscopy (TDS) method enabled by temperature programmed desorption, as well as by electrochemical hydrogen desorption methods.