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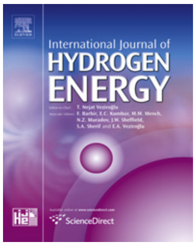

Influence of high pressure hydrogen on the tensile and fatigue properties of a high strength Cu–Al–Ni–Fe alloy

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ABSTRACT

Aluminum bronze CW307G was tensile and fatigue tested in 10 MPa hydrogen, 10 MPa helium and 0.1 MPa air atmosphere. Neither tensile nor S–N fatigue properties were affected when testing in H_2. Fractography on the fatigue specimens revealed similar striation morphology on the specimens tested in H_2 and He. Dissociative chemisorption as well as hydrogen absorption were identified as potential rate limiting processes being responsible for the impassivity to HEE of this alloy.

1. Introduction

Aluminum bronzes were developed primarily for marine applications due to their high tensile and fatigue strengths (comparable to low alloy steels) as well as their high corrosion resistances [1–5]. Due to this combination of properties, such alloys have been adopted for other engineering applications as well. Alloying with Al in the order of 10 wt% is mainly responsible for the excellent corrosion resistance and high strength. The main microstructural phase of such alloys is the fcc Cu rich α phase. Cu–10Al binary alloys suffer from the formation of brittle eutectoid phases limiting their technical use [3,4]. Alloying with Ni (about 5 wt%) retards this eutectoid formation [3] and further alloying with Fe (3–5 wt%) leads to the formation of fine dispersed Fe_3Al and NiAl type precipitates (so called κ-phases [5]) that usually do not tend to segregate at grain boundaries [3]. In principle, such multiphase aluminum bronzes are heat treatable. Quenching from elevated temperature produces an extremely hard and brittle martensitic structure (β-phase) and subsequent tempering may be used to produce the desired combination of strength and ductility [3]. Due to the poorer corrosion resistance of the β-phase, heat treatments are usually not performed for such alloys. A typical wrought Cu–10Al–5Ni–5Fe alloy is CW307G (UNS C63000, SAE CA630) which is standardized in EN 12163. In fuel cell vehicles (FCV), such alloys are sometimes used for parts requiring high strength and special magnetic properties.

In FCV applications, hydrogen environment embrittlement (HEE) is possible in all subsystems where H_2 has direct contact to metallic materials, especially the H_2 tank and its components like valves etc. Hydrogen embrittlement in known to occur in oxygen containing copper alloys [3] where H reacts with the cuprous oxide forming Cu and OH-reactants leading to severe embrittlement [3]. Although it is generally acknowledged that oxygen-free Cu alloys are not susceptible to HEE, very few data are available in the open literature,

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furthermore, the effect of alloying elements and microstructure is not investigated in detail. Pure OFHC copper [6–8] as well as some brass and bronze alloys [8–10] were tested in high pressure H_2 atmosphere without any reported reduction in ductility. However, for smooth bar tensile testing a change in fracture mode from cup and cone fracture (70 MPa air) to single shear lip fracture (70 MPa H_2) was reported [7]. The purpose of this investigation was to investigate the tensile and fatigue properties of CW307G in high pressure hydrogen atmosphere by means of tensile and S–N fatigue testing.

2. Experimental details

The chemical compositions of the 2 heats investigated here are tabulated in Table 1. Both heats were R740-treated by cold drawing (details see EN 12163). Heat 70 was used for tensile testing (ASTM G 142) whereas heat 74 was used for notched tensile testing and S–N fatigue testing (ASTM E 466). Smooth bar (specimen diameter 5 mm, gauge length 30 mm) and notched bar (outer diameter 8 mm, notch diameter 4–6 mm, notch radius 0.2 mm, notch angle 35°, stress concentration factor $k_t = 3.4$) tensile testing was performed in hydrogen (99.9999%) atmosphere at 10 MPa and 20 °C with a cross head speed of 0.1 mm/min (calculated strain rate of smooth specimens $\approx 5.5 \times 10^{-5}\ s^{-1}$). Reference testing was performed in air (0.1 MPa) with identical parameters. Identical notched specimens were used for S–N fatigue testing. Specimens were cycled until total failure in hydrogen and helium atmosphere (10 MPa, 99.9999%) at 20 °C, 1 Hz, R = 0.1 and triangular wave form. Reference testing was performed in air (0.1 MPa) with identical parameters. In the following graphs each data point represents one single test. All tests in H_2 atmosphere were performed at the Materials Testing Institute University of Stuttgart, Germany with a test apparatus described in [11]. Reference testing was performed at Materials Testing Institute University of Stuttgart and Opel Central Laboratories, Ruesselsheim, Germany.

3. Results and discussion

The microstructure of the Al-bronze investigated here is shown in Fig. 1. The very fine grained material (grain size about 5 μm = ASTM 12) consists of α phase (bright) and κ precipitates (dark) decorating the grain boundaries. The size of the larger κ precipitates was in the order of 1 μm.

The results of the smooth and notched tensile tests performed in 10 MPa H_2 atmosphere compared to those in air are shown in Fig. 2. None of the properties are degraded in H_2. This result was verified by SEM analysis of the fracture surface of the smooth specimens. Both the specimen tested in air as well as the specimen tested in H_2 showed microvoid coalescence on the entire fracture surface. Also, dissimilarities in microvoid size or shape could not be detected (Fig. 3a,b). When testing in H_2 atmosphere cracks usually start from the surface of the specimen. Therefore another characteristic of HEE is secondary cracking at the specimen gauge outer diameter. Some secondary cracks were detected on both specimens (Fig. 3c,d) but no differences were observed.

Table 1 – Chemical compositions of the 2 heats of CW307G (CuAl10Ni5Fe4) investigated here as given by the manufacturer's certificates.

Alloy ID	Al	Ni	Fe	Si	Mn	Zn	Cu
70	10,1	4,9	3,5	0,1	0,3	0,1	bal
74	10,9	4,6	4,6	0,0013	0.028	0,0065	bal

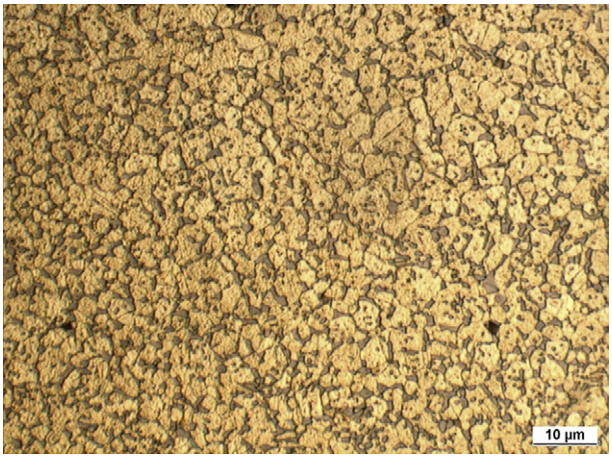

Fig. 1 – Microstructure of heat 70, Fe-III-chloride etchant. α phase (bright) and κ precipitates (dark).

The S–N curves of heat 74 tested in both air and H_2 are shown in Fig. 4. At the test parameters used here, fatigue strength exponents were similar in both atmospheres (−0.187 and −0.198) and numbers of cycles to failure were not reduced when testing in H_2 atmosphere.

Fractography was performed on specimens tested at $2S_a = 370$ MPa (Fig. 5) in air (N = 27978), He (N = 51639) and H_2 (N = 34814). In all atmospheres, crack propagation started from the surface until the remaining cross section failed due to overload. The crack propagation area was of comparable size (Fig. 5a–c) in all atmospheres. Fatigue fracture was characterized by transgranular fracture and no difference in such

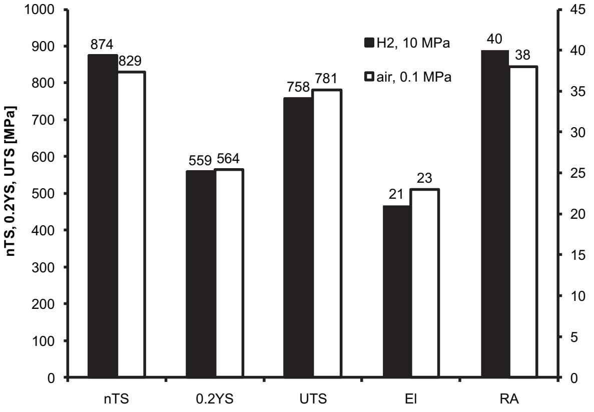

Fig. 2 – Results of notched and smooth tensile tests in high pressure hydrogen atmosphere compared to those in air. Notched specimens: nTS = notched tensile strength. Smooth specimens: 0.2 YS = 0.2 yield strength, UTS = ultimate tensile strength, El = elongation at rupture, RA = reduction of area.