INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 14887–14895

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

A thermodynamic approach for the development of austenitic steels with a high resistance to hydrogen gas embrittlement

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ARTICLE INFO

Article history:
Received 2 May 2013
Received in revised form
6 August 2013
Accepted 29 August 2013
Available online 7 October 2013

Keywords:
Gibbs energy
CALPHAD method
Hydrogen gas embrittlement
Austenite stability
Strain-induced martensite
Alloy development

ABSTRACT

The CALPHAD method was employed to assess the austenite stability of model alloys based on the Cr–Mn–Ni–Cu system. Stability was evaluated as the difference in Gibbs free energy between the austenite and ferrite phases. This energy difference represents the chemical driving force for the martensitic transformation and is employed as a design criterion. Six novel alloys featuring a lower driving force compared to the reference material AISI 316L were produced in laboratory. The susceptibility of all alloys to hydrogen gas embrittlement was evaluated by slow strain-rate tensile testing in air and hydrogen gas at 40 MPa and −50 °C. The mechanical properties and ductility response of four of the six alloys exhibited an equivalent performance in air and hydrogen. Thermodynamic calculations were in agreement with the amount of α'-martensite formed during testing. Furthermore, a 4.5 wt.% reduction in the nickel content in comparison to 316L promises a cost benefit for the novel materials.

1. Introduction

Implementation of a hydrogen economy is limited by the deleterious effect of hydrogen on the mechanical properties of most metallic materials. Since the ductility response is severely reduced by the presence of hydrogen, this phenomenon is usually referred to as hydrogen embrittlement (HE) [1]. If hydrogen arises from a gaseous environment, the resulting interaction is described as hydrogen gas embrittlement (HGE). Currently, high-alloyed austenitic stainless steels, such as AISI types 316 and 310, are selected for hydrogen applications owing to their high resistance to HE [2–7]. Nevertheless, the use of these types of alloys for hydrogen applications is restricted to prototypes or the discontinuous production of parts due to the high costs driven by the high nickel and molybdenum contents. Lowering the amount of nickel in these steel grades led to values ranging between 11.5 mass-% and 13 mass-%, which still results in a drawback concerning cost-efficiency [8–11]. Accordingly, novel alloys with equivalent properties but lower associated costs are needed for mass production of components, e.g. for hydrogen-powered cars.

There are few literature contributions that consider the economic aspects of HE-resistant materials. The systems Fe–22Cr–13Ni–5Mn [12–14], Fe–21Cr–6Ni–9Mn [12,13,15,16] and Fe–0.1C–10Mn–8Ni–2.5Al [17] are examples of such studies. These types of alloys either obey screening tests [12,13] or empirical developments [17]. Both methodologies are quite expensive in terms of time and financial resources. Therefore, the possibility of finding a design criterion to reduce time and expenses is of major interest for alloy

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0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2013.08.133

development. Since the ductility of austenitic steels in hydrogen decreases with increasing volume fraction of strain-induced α'-martensite [2–7,18], the design criterion used in this work was based on the tendency of the material to undergo this phase transformation. Technological features such as the geometry of segregations [9,19], heat treatments [20] and machining operations [21] also play an important role in the material's susceptibility to HGE. Moreover, the deformation mode of the alloy strongly influences the behaviour of the material in hydrogen [16,22,23]. Although all these features contribute to the loss of ductility in hydrogen, minimising the formation of strain-induced martensite has been identified as the first step to overcome in order to increase the resistance against HGE [4,18,24]. Furthermore, although designing a fully stable material does not guarantee a high resistance to HGE [23,25,26], no resistance to HGE can be expected if the alloy behaves in a metastable manner [5,18,26–28].

Based on preliminary investigations, a thermodynamic approach was implemented as a design criterion to define novel chemical compositions by means of computational thermodynamics prior to alloy production. Supported by the CALPHAD method, the driving force behind the martensitic transformation is evaluated as the difference in Gibbs free energy between the austenite and ferrite phases. This is interpreted in terms of austenite stability [29–31].

2. Experimental

2.1. Production of alloys

The novel alloys were produced in the laboratory via ingot casting in a vacuum induction furnace. As-cast ingots with a weight of 3 kg and a diameter of 50 mm were pre-machined to 42 mm and hot-worked in several passes to a final diameter of 16 mm. The as-forged bars were solution-annealed at 1150 °C, followed by water quenching. Tensile specimens with a gauge length of 30 mm and a diameter of 5 mm were produced by means of wet-turning, as described in [21]. The as-turned specimens were heat-treated in an industrial vacuum furnace at 1150 °C for 30 min and quenched with argon at a pressure of 200 kPa to avoid undesirable surface effects [21].

Semi-finished bars of austenitic stainless steel AISI type 316L, provided by Deutsche Edelstahlwerke (DEW, Germany), were employed as the reference material. Tensile specimens were machined out of the centre of 30 mm diameter bars, heat-treated in the same vacuum furnace for 30 min at 1050 °C and quenched with argon.

2.2. Testing

Tensile tests in air and in pure hydrogen gas (≥99.9999% H_2) were carried out at −50 °C with an initial strain rate of $5.5 \cdot 10^{-5}\ s^{-1}$ to account for the effect of temperature and strain rate on HGE susceptibility [27,32–34]. The selected parameters represent a condition of "maximum embrittlement" for most metallic materials [5,10,35,36]. Ambient pressure was used for the air-tested specimens, whereas 40 MPa was used for the tests in a hydrogen atmosphere. For hydrogen testing, the vessel was purged three times with pure nitrogen at 1 MPa, followed by eight consecutive purges with pure hydrogen at 1 MPa before filling to the test pressure. This procedure ensures safety and gas purity. In the hydrogen tests, the load was measured by an internal load cell in all cases. Clip gauge/extensometer measurements were used in air/hydrogen environments to determine the 0.2% proof stress. A total of four tests were performed on every alloy: two in air and two in a hydrogen atmosphere. The measured properties were yield strength ($Rp_{0.2}$), ultimate tensile strength (R_m) and elongation to rupture (A). Additionally, the reduction of area (Z) was obtained *ex situ* by measuring the initial and final diameters of the specimen at the necking circumference with a digital calliper. The Z parameter is known to be very sensitive for qualifying the susceptibility of metallic materials to HGE [5,26,37].

The ferrite equivalent value of every specimen after tensile testing was also obtained *ex situ* by means of a FeritScope® MP30 device (Helmut Fischer GmbH, Germany). This value was obtained as the average of four measurements radially distributed at the midpoint of the uniformly elongated region and represents the amount of material that undergoes a $\gamma \rightarrow \alpha'$ martensitic transformation [38]. Moreover, digital microscopy was implemented to evaluate the fracture surfaces and necking regions of the as-tested specimens at a magnification of 50×. The latter was performed using a VHX-600D digital microscope (Keyence GmbH, Germany).

3. Design criterion and results

3.1. Preliminary results on the thermodynamic stability

The susceptibility of austenitic steels to HGE is frequently related to the stability of the austenitic phase against the α'-martensite transformation [2–5,27,28]. Such stability can be assessed experimentally by empirical formulae or by thermodynamic calculations [5,39,40]. Previous investigations on HGE of modified AISI type 304 steels established a relationship between the loss of ductility in hydrogen and the thermodynamic stability of the austenite phase [26]. Equation (1) was used to evaluate the thermodynamic stability, which represents the chemical driving force for the martensitic transformation [29–31]. The obtained parameter, $\Delta G_{\gamma/\alpha}$, allows a direct comparison of different alloys: the higher the absolute value of $\Delta G_{\gamma/\alpha}$ is, the higher is the chemical driving force available for the martensitic transformation. The results obtained in [26] are summarised in Fig. 1 and are based on the compositions and properties presented in Table 1. Fig. 1 depicts the reduction of area in hydrogen (Z_{H_2}) and the ferrite equivalent fraction in air of three alloys: a low-manganese 304 steel (304_{Mn}), a high-molybdenum 304 steel (304_{Mo}) and a 316L steel [26]. Magnetic response measurements performed *ex-situ* on the uniform elongated area of air-tested tensile specimens showed a marked difference in the corresponding ferrite equivalent fraction (F.E. in Fig. 1). Such values are representative of the material's volume fraction that transforms to martensite upon deformation [17,26,38]. Since the three alloys undergo a uniform elongation of $A_{g-air} \approx 53\%$ (Table 1), an equivalent mechanical driving force for the martensitic transformation is expected in the three materials. Therefore,