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Testing of welded 2.25CrMo steel, in hot, high-pressure hydrogen under creep conditions

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Abstract

The standard 2.25Cr–1Mo steel, has been used for most of the hydroprocessing reactors built during the 30 years up to the end of the 1990's. Under service conditions, the steel, and in particular its weldments, may experience degradation by ''hydrogen attack'', or high-temperature hydrogen attack (HTHA), which is responsible for several failures and even casualties occurring in the history of the industry. The selection of the structural steels is still based on the empirical Nelson curves which, among other limitations, do not provide information on the behaviour of weldments. This causes uncertainties in the definition of the safety boundaries for operation of pressurized components in the petrochemical industry. The results of the present study confirm that weldments are a weak point of the pressurized components and suggest that the HAZ, and in particular the ICHAZ, is the most sensitive metallurgical zone to hydrogen attack.

Keywords: Weldments; ICHAZ; Type IV; Hydrogen attack; 2.25Cr–1Mo steel pipe

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1. Introduction

Pressurized components of electricity generating stations and petro-chemical plants operate for long periods at temperatures where creep may occur. The majority of service failures of industrial equipment made of Cr-Mo steels have been reported to occur in critical parts such as welds, mainly due to the microstructural changes, due to the composition of the alloy in use and to the thermal fields produced by the welding process [1], which give rise to marked variations in the material properties [2]. Particular processes such as hydrocracking, desulphurisation, hydrogen treating and chemical synthesis of ammonia operate in conditions where the structural steels of hydroprocessing equipment are exposed to high pressures of hydrogen at temperatures above 573 K (300 °C). The structural steels of hydroprocessing equipment may appear unaffected for long periods, even for years, then, in a relatively short time, they can exhibit degradation of mechanical properties, mainly toughness and ductility, and, as a consequence, fail without warning [3]. The cause of this behaviour is

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a degradation phenomenon called "hydrogen attack", or high-temperature hydrogen attack (HTHA) which produces an irreversible damage [4] and arises from the nucleation, growth and coalescence of methane bubbles to form fissures, mainly along the grain boundaries [5].

Early fundamental work on this subject [6] pointed out that the main aspects of the damage are: loss of strength and ductility, decarburization, formation of microscopic cracks and fissures, blistering, which are caused by the formation of methane after the reaction of hydrogen with the carbon of the steel (methane reaction). Hydrogen attack leads to both surface and internal decarburization. The former is encountered on the surfaces directly exposed to hot-high pressurized hydrogen, and leads to the formation of a decarburized layer whose thickness depends upon: the operational (or testing) conditions; the composition of the steel; the history of the steel (treatment received, eventual cold work, etc.); the geometry of the component (e.g. the thickness); the surface finish. The latter leads to methane filled bubbles, whose growth is driven by the methane pressure and may link-up into fissures [7–9]. It is mainly the bulk decarburization that compromises the integrity of the components due to the formation along the grain boundaries of the bubbles which endangers safe operation. In this way, the industrial failures due to hydrogen attack are an integral part of the wider category of failures due to hydrogen damage, where related accidents have been estimated to cost equivalent to about 100 billion dollars/year in the USA and are responsible for several deaths and many injuries of workers [10,3].

The basis of the steel selection for the design of equipment operating in the presence of hot, high-pressure hydrogen, are the Nelson curves, published for the first time in 1951. They collect data available from industrial experience and indicate the pressure–temperature ranges in which certain steels, but not their weldments, may be used without experiencing hydrogen attack [11]. Selected on the basis of its overall characteristics, the standard (or conventional) 2.25Cr–1Mo steel, had been the material used for most of the hydroprocessing reactors built during the 30 years up to the end of the 1990s. It is evident that the petrochemical sector has amassed a wide experience of the performances of 2.25Cr–1Mo in the current hydroprocessing conditions. Nevertheless the knowledge about the in-service behaviour of this alloy's weldments is still incomplete and limited data are available in the literature on the behaviour of welded joints in hot high pressurized hydrogen, especially in presence of complex states of stresses. These needs led several partners, representative of all the chain, from the steel producer to the end user (the petroleum companies), to integrate their research efforts in the Brite/Euram Project 1835 (PREDICH) [12]. The aim of this European consortium, led by Usinor Industeel, was to acquire data for the evaluation of the lifetime of pressure vessels made with conventional and new steels. The present work was carried out in the frame of the JRC contribution to this project.

2. Experimental

2.1. Materials

The material used for the present investigation was received from USINOR Industeel, in the form of a square-base coupon, approximately 80 mm × 80 mm × 400 mm, with the weldment at mid-length. The coupon was part of a batch tested by the partners of the PREDICH project. Data on nominal composition for both the base metal and the flux-and-wire combination, used as a consumable for the submerged-arc-welding (SAW) process, are given in Table 1, compared with the results of EPMA analysis carried out at the JRC/IE. The base metal (BM) had been water quenched from 1213 K (940 °C), and tempered at 923 K (650 °C). The post weld heat treatment (PWHT) consisted of 30 h at 963 K (690 °C).

Table 1
Nominal composition of the 2.25Cr–1Mo steel and consumable compared with EPMA (mass%)

Sample		C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	Sn
BM	Nominal	0.14	0.18	0.59	0.004	0.003	2.25	1.05	0.14	0.01	0.07	0.006
	EPMA	–	0.18	0.62	–	–	2.09		0.13	–	0.08	–
Consumable	Nominal	0.10	0.11	0.75	0.009	0.002	2.37	1.01	0.11	–	–	0.002
	EPMA	–	0.11	0.77	–	–	2.03	1.09	0.14	–	0.09	–