Materials Science & Engineering A 725 (2018) 88–97

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Detection of intergranular embrittlement of reactor pressure vessel steel by electrochemical method

Tenneti Sharma[a,b], Sunil Kumar Bonagani[c], N. Naveen Kumar[c], I. Samajdar[d], V. Kain[a,c,*]

[a] Homi Bhabha National Institute, Trombay, Mumbai 400085, India
[b] Indian Navy, India
[c] Materials Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[d] Department of Metallurgical Engineering & Materials Science, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

ARTICLE INFO

Keywords:
Low Alloy Steel
Aging
Impact Toughness
Carbide precipitates
Segregation
Electrochemical polarisation test

ABSTRACT

The reactor pressure vessel (RPV) steel, with manganese-nickel-molybdenum (Mn-Ni-Mo) alloying, was subjected to accelerated thermal aging treatment at 450 °C for durations upto 8400 h. Impact toughness decreased and the intergranular fracture (IGF) increased monotonically with increased aging time. This was accompanied by insignificant changes in average hardness, grain size, misorientation and carbide size. However, electrochemical polarisation tests in picric acid showed increasing width of attack at prior austenitic grain boundaries (PAGB). It was hypothesized that the accelerated aging led to phosphorus segregation at the grain boundary, a hypothesis supported by the post electrochemical attack on the PAGB, leading to a significant loss in impact properties.

1. Introduction

Low Alloy Steels (LAS) are used as the structural material in fabrication of the nuclear reactor pressure vessel (RPV) due to the excellent high temperature mechanical properties it provides and its compatibility in the operating environment of the reactor. The nuclear RPV is exposed to neutron fluence in addition to the prolonged high operating temperature it sees all along the operation life of the reactor. These steels are also exceedingly sensitive to heat treatments that are a part of the fabrication processes [1] and the resulting microstructures have a wide scatter in the desirable properties. Since the life of the nuclear plant is decided by the RPV, understanding its microstructural evolution that takes place during fabrication and subsequently degradation during its operation is of paramount importance. Measuring the degradation and assessing the residual life of the material is essential to ensure safe plant operation and also to extend the life of the plant beyond the design life.

The two major types of steels used worldwide for construction of RPVs are Mn-Ni-Mo steels (commonly referred to as western type RPVs) and Cr-Mo-V steels (commonly referred to as eastern type RPVs) [2–4]. Grades 15Kh2NMFAA and 15Kh2MFA [5] are examples of eastern grade RPV steels and 20MnMoNi55, SA508 grade 3, SA533, SA 302B are some of the grades of western RPVs [2–4,6,7]. The RPV materials having ferritic/ferritic-bainitic microstructure [4] (or body centered cubic (bcc) crystal structure) show the typical ductile to brittle transition (DBT) phenomena (Fig. 1) [2]. At low temperature the bcc materials show low impact toughness while at room temperature or higher temperatures, these materials show high impact toughness (Fig. 1). The transition from low to high impact toughness with increase in temperature (typical S curve) is characterized by ductile to brittle transition temperature (DBTT) that is typically taken as the middle point between the high and the low plateau of toughness. Irradiation shifts the typical S curve to right side and lowers the upper shelf impact energy drastically (Fig. 1). Radiation embrittlement (RE) manifests as lowering of upper shelf energy and DBTT shift to higher temperature. Both western and eastern materials have distinguishable chemical compositions and thus it is expected that their response to the radiation embrittlement is also different. Though the radiation embrittlement of both types of the steels depends on the operating fluence, the major factor governing the irradiation sensitivity is the amount of the deleterious elements present. The main elements identified to contribute to RE are phosphorus (P) and copper. Nickel has also been reported to increase the irradiation damage sensitivity caused by copper [2].

The primary mode of degradation of the properties of the RPV steels is radiation embrittlement. Three basic mechanisms are considered to contribute to radiation embrittlement: (a) direct matrix damage by high energy neutrons, (b) irradiation-induced precipitation and (c) element segregation [8,9]. The effect of these three components to the overall

---

[*] Corresponding author at: Homi Bhabha National Institute, Trombay, Mumbai 400085, India.
E-mail address: vivkain@barc.gov.in (V. Kain).

https://doi.org/10.1016/j.msea.2018.04.008
Received 21 January 2018; Accepted 3 April 2018

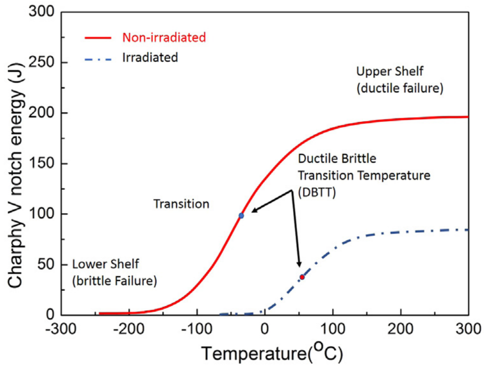

Fig. 1. Effect of irradiation on ductile to brittle transition temperature (DBTT) and upper shelf energy for ferritic steels.

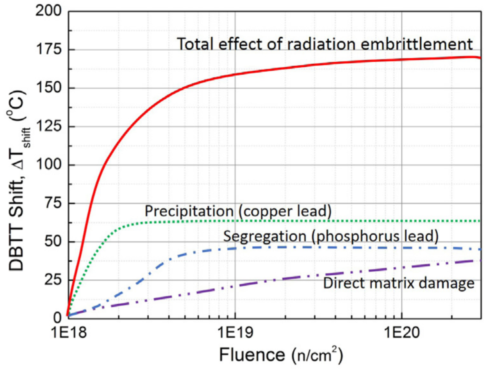

Fig. 2. Three components of radiation embrittlement for RPV steels, as a function of neutron (energy > 0.5 MeV) fluence [8].

degradation is additive. Formation of radiation induced precipitates/segregates (Cu-rich, may contain Ni also) and radiation defects in the steel matrix are hardening mechanisms resulting in increase in the yield strength and are primarily due to these features acting as obstacles for dislocation movement. The non-hardening mechanism of embrittlement comprises impurities segregation (primarily P) at grain boundaries and interfaces [10]. The presence of P at the grain boundary lowers the cohesion energy causing the material to fail through intergranular mode [3]. This is taken to be due to changes in local electron density and weakening of base material atomic bond energy [4]. The effects of precipitation and segregation are found to saturate with time whereas the direct matrix damage continues to increase all along its lifetime as shown in Fig. 2. [8].

Though most of the degradation in the properties is due to irradiation, thermal aging is known to contribute to these effects [11]. Corwin [12] brought out that a number of processes, viz., formation of hardening phases (such as copper-rich precipitates (CRP)) and segregation of P lead to the embrittlement of RPV steels subjected to long-term service at elevated temperatures. These processes are accelerated or enhanced due to irradiation. Pure thermal aging represents a zero-flux limit of damage rate-dependent effects [6]. Thermal ageing is a temperature, material state (microstructure) and time dependent degradation mechanism [6]. The degradation in the properties when LAS components are subjected to elevated operating temperatures is primarily of two types: (a) due to changes in microstructure and /or (b) due to diffusion of impurities such as P, Sn, As, and Sb to the grain boundaries/interfaces [13–15]. The changes in microstructure, such as carbide coarsening and precipitation of more stable carbides during service, can cause softening and irreversible embrittlement. Also carbide coarsening and precipitation of more stable carbides causes lowering of impact energy although there is reported to be no effect on DBTT [13]. In contrast, segregation of impurities at the grain boundaries results in temper embrittlement of these steels that does not affect the hardness and increases the DBTT but is reversible [13]. Cr-Mo steels are shown to be largely susceptible to degradation by carbide coarsening and Cr-Mo-V steels by segregation to grain boundaries [16]. Takahashi et al. [17] have shown P segregation in Cr-Mo (2.25 Cr-1Mo) and Cr-Mo-V steels. In the case of X20CrMoV12.1 alloy steel pipe, it was shown that the degradation of the material is mainly related to carbide coarsening [18].

The effects of thermal aging on the degradation of the properties have been studied by many. There is literature to suggest that the degradation effects of thermal embrittlement are negligible whereas a few researchers have suggested otherwise also. The effects of long-term aging at temperatures up to 350 °C (reactor operating temperature) on the ductile-to-brittle transition temperature of RPV steels have been studied by Corwin et al. [12]. Corwin et al. showed from literature data that there is no embrittlement at such reactor operation temperatures for operation periods of up to 100,000 h [12]. Similarly, DeVan et al. [19] reported that DBTT of RPV steel from the Arkansas 1 reactor shifted from − 1 to 9 °C after thermal ageing at 280 °C for 93,000 h. The material from the beltline region of the Oconee Unit 3 reactor showed an increase of about 1 °C after exposure to a temperature of 282 °C for 103,000 h [19]. Fukakura et al. [20] studied the effect of thermal aging on western grade RPV steel and concluded that after thermal aging for 10,000 h at temperatures of 350 °C, 400 °C and 450 °C, the increase in the DBTT was small.

In contrast, P segregation due to thermal aging at higher temperatures has been confirmed by various studies. Gurovich [21], while investigating both eastern and western steels has attributed an essential part of the RE to P segregation to interfaces. The investigation by Oleg Zabusov [22] showed that continuous exposure of VVER-1000 RPV material at 320 °C caused an increase in P content at grain boundaries. It was observed that this effect could be due to the presence of carbides at the grain boundaries with increased P content at the carbide/matrix interface and lead to intergranular embrittlement of unirradiated RPV components by the end of the extended service life. Yaroslav I. Shtrombakh et al. [11] analysed VVER 1000 RPV steel (base material and welds) and found that found that during long term exposures at operating temperatures of 310–320 °C, thermal aging effects are observed only when the Ni content is high and are the result of the grain boundary segregation. Pierre et al. [23] has shown a shift in DBTT of 37 °C in 18MND5 (composition very close to 16MND5 grade used for RPVs) steels after thermal aging at 450 °C for 5000 h due to P segregation to grain boundaries. Antoine Andrieu et al. [24] using a mathematical model, has reconfirmed the DBTT shift of 40 °C in Mn-Ni-Mo steels due to thermal ageing at 450 °C for 5000 h. Broughton et al. [25] studied the changes in the grain boundary chemistry of D6ac (Ni-Cr-P) steels with heat treatments and found P concentrations at the grain boundary increased rapidly during the initial stages of ageing to reach a plateau level at 480 °C and a maximum value at both 520 and 560 °C. In a similar study of A533B plate [26] and A508 [27] forging materials, Druce et al. [28] studied the effects of thermal ageing in the temperature range 300–550 °C for durations up to 20,000 h and showed that ageing increased the DBTT by an amount dependent on the material, prior heat treatment, ageing temperature and time. The embrittling/segregation potency of P was highly dependent on prior heat treatment; highest in the coarse-grained, higher hardness simulated HAZ condition, and the least in the conventionally quenched and tempered condition.

Degradation in the material by formation and evolution of the carbides has also been widely reported. Nishizaka et al. [29] and Qu and Kuo [30] have shown that service-exposed Cr-Mo (reactor pressure vessel) and 2.25 Cr-Mo-V(steel bolts) embrittle due to precipitation or change in morphology of carbides during service. Williams and Wilshire [31] have further shown a progressive loss of the creep resistance of a 0.5Cr-0.5Mo-0.25V steel before and after service at elevated temperatures decreased with increasing intercarbide particle spacing and with