Materials Characterization 57 (2006) 274 – 280

MATERIALS
CHARACTERIZATION

The effect of microstructural evolution on hardening behavior of type 17-4PH stainless steel in long-term aging at 350 °C

Jun Wang [a,b,*], Hong Zou [b], Cong Li [b], Shao-yu Qiu [b], Bao-luo Shen [a]

[a] *School of Materials Science and Engineering, Sichuan University, Chengdu, 610065, PR China*
[b] *Nuclear Power Institute of China, Chengdu, 610041, PR China*

Received 21 December 2005; accepted 4 February 2006

Abstract

The effect of microstructural evolution on hardening behavior of 17-4PH stainless steel in long-term aging at 350 °C was studied by X-ray diffraction and transmission electron microscopy. The results showed that there is the matrix of lath martensite and nanometer-sized particles of ε-Cu precipitated from the matrix after the alloy is solution treated and tempered. When the alloy was aged 350 °C for 9 months, α-α′ spinodal decomposition occurred along the grain boundaries and caused an increase in hardness which compensated for the weakening effect due to ripening of the ε-copper precipitates. Upon further aging to 12 months, the Cr-rich α′-phase and $M_{23}C_6$ precipitated, both of which strengthened the alloy considerably and led to enhanced hardening despite the continued softening by overaging of the ε-copper precipitates. With the aging time extended to 15 months, substantial reversed austenite transformed and precipitation of the intermetallic G-phase occurred near the ε-Cu precipitates in the matrix. The abundant amount of reversed austenite that transformed led to rapid softening.

Keywords: 17-4PH stainless steel; Isothermal aging; Microstructure evolution; Hardness; Reversed austenite; Spinodal decomposition; G-phase

1. Introduction

17-4 precipitation hardening (17-4 PH) stainless steel is widely used as a structural material for chemical and power plants, such as light water reactors (PWRs and BWRs) due to its favorable combination of excellent mechanical properties and good corrosion resistance [1–4]. These materials are required to remain in service for very long periods of time; hence, understanding the microstructural evolution at the service temperature is very important. Typical service temperatures in power plant applications are about 300 °C [2].

The material conditions described as H900 (peak-aged condition) and H1100 (over-aged condition) of this precipitation-hardenable stainless steel are commonly used. In the past, the H900 condition was more popular due to higher strength, but recently some researchers have reported a greater tendency to embrittlement in this condition under certain working conditions [5–7]. For that reason it is common to see this material used in the H1100 condition for LWR reactor applications, owing to the requirements of high wear resistance, high strength, and good corrosion resistance [8].

According to the solid state miscibility gap in Fe–Cr phase diagram [9], the Cr concentration in 17-4 PH is within the spinodal line, in which phase decomposition of the martensite into the Cr-rich α′ and Fe-rich α phases is expected on aging below 450 °C. Considerable

---

[*] Corresponding author. School of Materials Science and Engineering, Sichuan University, Chengdu, 610065, PR China. Tel./fax: +86 28 8540 2231.

E-mail address: srwangjun@163.com (J. Wang).

1044-5803/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.matchar.2006.02.004

research has been carried out on spinodal decomposition in this alloy [10–12]. However, earlier investigations using transmission electron microscopy (TEM) failed to reveal the detailed nanometer-scaled structure and chemistry of the spinodally decomposed microstructure of this alloy [9–11]. Recently, employing an atom probe, Murayama has seen evidence of spinodal decomposition of 17-4PH SS but failed to resolve the finer scale of the microstructure [12]. Danoix estimated the corresponding activation energy for the spinodal reaction, $Q=230$ kJ/mol, which is in very good agreement with the activation energy for chromium diffusion in α-iron [4]. This value for the activation energy was very similar to that obtained by Leax et al. [13].

Some studies on the effect of long-term intermediate temperature aging of 17-4PH stainless steel suggested the G-phase, an intermetallic compound, commonly precipitated in association with the spinodal decomposition [5–8,14]. But the relationship of G-phase to other precipitates and to the matrix is unclear [11]. Leax et al. calculated an activation energy for G-phase precipitation of 140±60 kJ/mol, which was about half of that measured for α-α' decomposition [13].

Reversed austenite transformation is a common phenomenon in martensitic PH stainless steels aged at intermediate temperatures [15–17]. Generally, the Johnson-Mehl equation can be used to describe the progress of the reverse austenite transformation, which is a diffusion-controlled precipitation reaction [17]:

$$y = 1 - e^{-(kt)^n}$$

where y, t, k and n are the volume fraction transformed, the aging time, constant for a given temperature and the time exponent, respectively.

Nakagawa reported an activation energy for the formation of reversed austenite as 240 kJ/mol, which is very close to the value for the diffusion of Ni in ferrite, 245 kJ/mol, and suggested the formation process for austenite reversion was controlled by the diffusion of Ni in the martensite matrix [17]. Balan found the fine-scale reversed austenite precipitation may cause a hardening effect [15], but Nakagawa [17] and Ping [16] suggested it would lead to softening.

More recently, some work was performed about the effect of thermal aging on the properties of martensitic PH stainless steels [1–4,11,19,20]; the research reported in [2,11,18] emphasized the effects of long time aging at intermediate temperature. Christien found a large shift in the ductile-to-brittle transition temperature (DBTT) of 17-4PH after aging 15,700 h at 320 °C [18]. The author calculated the dynamic fracture toughness change with aging time at 350 °C by means of an instrumented impact test, and got the experimental formula [2]:

$$\mathrm{K_{Id}} = 30.57 + 235.76 \cdot \exp\left(\frac{-t}{1326.65}\right)$$

where t is aging time.

However, this previous research does not clarify the relationship between microstructure evolution and a number of properties, especially hardness. The aim of the present work was to try to investigate the hardening behavior, and to characterize microstructural transformations in 17-4PH stainless steel aged more than 10,000 h at 350 °C, which is slightly above the service temperature, in order to enhance the microstructure evolution. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to examine and elucidate the microstructural development.

2. Experimental procedure

The chemical composition of 17-4PH stainless steel is given in Table 1.

The material was procured as hot rolled 20-mm sheet, in an L-T (longitudinal–transverse) orientation; this sheet was subsequently cut into specimens with the dimension of 10×10×55 mm.

Heat treatment consisted of two steps:

(1) Solution treatment for half an hour at 1040 °C and then oil quench;
(2) Temper (precipitation) treatment for 4 h at 595 °C and then air cool.

The bulk hardness was measured using a Rockwell hardness tester with a load of 150 kg (HRC). The temper treated alloy sample was held in an oven-type furnace at 350 °C for times exceeding 10,000 h and then subjected to microstructure analyses. The content of the austenite was determined using XRD, with an X'Pert Philip X-ray

Table 1
Composition of type 17-4PH stainless steel (mass%)

Elements	C	Si	Mn	P	S	Cr	Ni	Cu	Nb	Fe
mass%	0.04	0.6	0.3	0.023	0.013	16.39	4.32	3.4	0.36	Bal.