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Short Communication

An electrochemical method for detection and quantification of Laves phase in 12Cr martensitic stainless steel

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ABSTRACT

An electrochemical method for the detection and quantification of Laves phase in 12Cr martensitic stainless steel is proposed in the present work. Laves phase dissolution peak can be observed at the lower potential range which can be obtained in anodic polarization curves in a specific solution with specific pH values. The amount of Laves phase was calculated by the integration of anodic current with time according to the polarization curve and also independently measured by using scanning electron spectroscopy. A good correlation of these two methods was obtained.

1. Introduction

12Cr martensitic steel is a common heat resistant alloy which has been widely used in ultra-supercritical power plant for its excellent creep resistant property at a temperature range of 600 °C. However, after a long-term exposure to the high temperature operational environment, some metallurgical degradation takes place and detrimental phases, such as Laves phase, can precipitate, which plays a key role in the ageing degradation in terms of embrittlement and also creep damage accumulation of the materials [1–7]. The quantification of Laves phase in heat resistant alloys has been studied mainly by morphological observation through electron microscope in the past as can be seen in the literatures [8,9]. However, such studies were usually time-consuming and the analyzed area was very limited. In recent years, some electrochemical methods were developed to detect the precipitates in heat resistant alloys [10,11]. However, these studies could neither discriminate Laves phase from other precipitates nor accurately quantify its amount.

The objective of the present study is to develop a novel electrochemical technique to detect and quantify the amount of Laves phase. In this paper, appropriate possible solutions for this purpose have been examined and consequently the selective dissolution current peak of Laves phase was successfully discriminated from the matrix and other precipitates, and the amount of Laves phase was precisely quantified.

2. Material and methods

The material used in this work is 12Cr martensitic steel. Table 1 shows the chemical composition. The material was quenched after a solid solution treatment at 1070 °C, tempered at 570 °C and second tempered at 700 °C. Then the material was aged for different time at 630 °C to simulate the ageing degradation during service operation. The specimens after quench, quench/temper and with different ageing time were designated as Q (quenched), QT (quenched and tempered) and A1–A6 (ageing time:1400 h, 2800 h, 5600 h, 10000 h, 15000 h and 20000 h, respectively). The electrochemical tests were performed by using POTENTIOSTAT/GALVANOSTAT HAB-151A electrochemical workstation. A three-electrode cell consisting of two carbon rods as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode were used in this test. Before the electrochemical test, all the specimens were ground to 1000 grit and then sealed by epoxy resin. In order to examine the electrochemical possibility of selective dissolution of Laves phase, potentiodynamic polarization curve measurements were conducted in 0.086 mol/L (pH = 12.9), 0.86 mol/L (pH = 13.9), 1.72 mol/L (pH = 14.2) and 4.3 mol/L (pH = 14.6) KOH solutions with a sweep rate of 10 mV/min. All the solutions were deaerated by N_2 before and during the tests. In all measurements, a potential scan started after an open circuit potential (OCP) stabilized. It was found more than 90% Laves phase was dissolved under a sweep rate of 10 mV/min by one-time scanning in deaerated 4.3 mol/L KOH solution. To guarantee a high efficiency and accuracy of the quantification of the

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Table 1
The chemical composition of 12Cr stainless steel (wt.%) used in this work.

C	Si	Mn	Cr	Mo	Ni	W	V	Nb
0.12	0.06	0.43	10.3	1.05	0.78	0.96	0.18	0.05

amount of Laves phase, 10 mV/min was selected as the sweep rate. To clarify the meaning of current peaks obtained in potentiodynamic polarization curves, potentiostatic etching tests were performed on A6 at some selected potentials for 20 min. All the polarization curve measurements were conducted 3 times each to clarify the reproducibility.

Before the observation of the microstructure, the material etching was conducted with an etchant of 1 g picric acid + 5 ml hydrochloric acid + 100 ml ethanol for 30 s before observation. The microstructure of the alloy and the surface morphology changes before/after the potentiostatic etching were examined in the same areas by scanning electron microscope (SEM, Hitachi SU70) in backscattered electron (BSE) mode. The morphology and composition of the precipitates in A6 were examined by Auger electron spectroscopy (AES, PHYSICAL ELECTRONICS PHI 680 Auger Nanoprobe), Transmission electron microscope (TEM, TOPCON EM − 002B) and Energy dispersive spectroscopy (EDS, Thermo Fisher Scientific Noran System 6).

To verify the accuracy of the electrochemical method for detection and quantification of Laves phase, the area fraction of Laves phase in different specimens was also analyzed by using SEM under BSE mode. Digital images consisting of 1280 × 960 pixels were used. For better accuracy of area measurements of precipitates, the smallest detectable particle size was considered to be approximately 20 pixels and particles smaller than this size were ignored from the results, which means the equivalent diameter below approximately 15 nm was not taken into consideration. BSE images were used to identify the Laves phase from carbide due to the larger atomic number contrasts. At the same time, because there is a larger measurement depth of the BSE images, SE images on the same area were observed to assess the accurate shape of the Laves phases to avoid the under- or over-estimation of the particle size. 30 adjacent images were taken in each mode at the same area under all the conditions and the total analyzed area for each specimen was about 3500 μm^2. The commercial software ImageJ was used to calculate the area fraction of Laves phase.

3. Results

3.1. Characterization of Laves phase by using electron spectroscopy

Fig. 1a shows the microstructure of A6 after the etching, where a typical tempered martensitic structure is observed as have been done in the previous studies [12,13]. Fig. 1b shows the microstructure of the same area but observed by BSE mode. Numerous precipitates are observed. In order to identify these precipitates, TEM analysis with EDS was conducted as shown in Fig. 1c. Two kinds of precipitates with different sizes can be typically observed. Large precipitates (~ 1 μm) with an irregular shape are enriched in W and Mo, which is a typical feature of Laves phase in Fe-based alloys [14,15]. It is worthy to note that the atomic ratio of (Fe, Cr) and (Mo, W) is basically 3: 1, which is higher than the typical Laves phase ratio (A_2B). The difference may be caused by the nonstoichiometric feature of Laves phase, which has been reported by many researchers. Fine precipitates (less than 200 nm) with a spherical shape are enriched in Cr, which are deemed as carbides [14].

To examine the elemental concentration in the Laves phase precipitates, AES mapping was performed and the result on A6 sample is shown in Fig. 2. Large Laves phase particles with an enriched Mo and W content are observed. At the same time, numerous small precipitates (carbides) are also detected, which contain a higher C and Cr content. This result agrees well with the TEM-EDS analysis.

Fig. 3 demonstrates the growth of Laves phase with the increment of ageing time, where an area fraction of Laves phase measured by SEM observation are plotted as a function of ageing time. It is clear that the amount of Laves phase increases as ageing time increases.

3.2. Identification of the selective dissolution of Laves phase

Potentiodynamic polarization curves were measured on the sample of A6 in the deaerated KOH solutions with different concentration and results are shown in Fig. 4. As can be seen clearly, only one current peak in each measurement in KOH solutions with concentrations of 0.086 mol/L, 0.86 mol/L and 1.72 mol/L was observed. Typical potential, for example of the peak current is around 0.31 $V_{Ag/AgCl}$ in 0.086 mol/L KOH solution and the peak potential shifts towards the negative direction gradually with the increment of KOH concentration. This selective dissolution behavior has been reported by other researchers and is attributed to the dissolution of carbides [16] or Cr, Mo enriched phase [10]. In this paper, this peak is named as “peak 1”. It is worthwhile and unique to observe another anodic current peak in the polarization curve measured in deaerated 4.3 mol/L KOH and the peak current appears at the potential of $-0.55\ V_{Ag/AgCl}$ besides the peak 1, namely 0.09 $V_{Ag/AgCl}$ in this case. This selective dissolution at the lower potential of $-0.55\ V_{Ag/AgCl}$ is firstly observed in this work and is interesting to examine the cause of this dissolution behavior. In this study, this new peak is named as “peak 2”. At the end of all the polarization curves measurement, the potential reaches to the one where a current increases sharply caused by the oxygen evolution.

Based on the polarization curves in Fig. 4, potentiostatic etching was performed at the potential of 0.31 $V_{Ag/AgCl}$ in 0.86 mol/L and $-0.55\ V_{Ag/AgCl}$ in 4.3 mol/L KOH on A6 sample and results are shown in Fig. 5. Fig. 5a shows the precipitates morphology of A6 measured by BSE mode before potentiostatic etching in 0.86 mol/L KOH solution. Only white precipitates with sizes around 1 μm can be observed along the grain boundary and in grains on the surface, which are mainly Laves phases. It should be noted that fine precipitates of carbides shown in Fig. 1c and Fig. 2 are invisible due to less deviation in atomic number from the matrix. Fig. 5b shows the precipitate morphology after potentiostatic etching at 0.31 $V_{Ag/AgCl}$ (peak 1) in the same area. Comparison of Fig. 5a and b clearly indicates that Laves phase did not dissolve after etching under such condition. However, many tiny holes in grains and along the grain boundaries appear, which would be formed by dissolution of fine intragranular carbides and large intergranular carbides. Similar observation has been reported in Refs. [11,16]. Fig. 5c and d show the SEM images (BSE mode) before and after potentiostatic etching at $-0.55\ V_{Ag/AgCl}$ (peak 2) in 4.3 mol/L KOH solution. Only Laves phase dissolved after potentiostatic etching under this condition, which demonstrates the new peak (peak 2) in 4.3 mol/L KOH solution corresponds to the dissolution peak of Laves phase. It is worthy to notice that several Laves phase particles can still be observed in Fig. 5d. This is because the penetration depth of the BSE can be hundreds of nanometers and these Laves phase particles observed are beneath the surface and cannot be dissolved by etching.

3.3. Quantitative analysis of Laves phase amount

After clarifying the meaning of peak 2 in Fig. 4, the amount of Laves phase can be determined quantitatively by the charge of this dissolution peak in the potentiodynamic polarization curve, assuming that all the Laves phase particles are dissolved after the peak 2.

Cyclic anodic polarization curve measurements were conducted in deaerated 4.3 mol/L KOH solution. As shown in Fig. 6, the polarization curves were successively measured three times where the first measurement was started from OCP to the potential over peak 2 of about $-0.35\ V_{Ag/AgCl}$ followed by the second measurement starting from the corresponding OCP after the first measurement, which is about $-0.9\ V_{Ag/AgCl}$ to about $-0.35\ V_{Ag/AgCl}$. It is clear that peak 2 in the