Scripta Materialia 121 (2016) 37–41

Contents lists available at ScienceDirect

Scripta Materialia

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

Regular Article

Three dimensional atom probe and first-principles studies on spinodal decomposition of Cr in a Co-alloyed maraging stainless steel

Jialong Tian [a,c], Wei Wang [a,*], Lichang Yin [a,b,*], Wei Yan [a], Yiyin Shan [a], Ke Yang [a]

[a] Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
[b] Shenyang National Laboratory for Materials Science, 72 Wenhua Road, Shenyang 110016, China
[c] School of Materials and Metallurgy, Northeastern University, Shenyang 110004, China

ARTICLE INFO

Article history:
Received 5 January 2016
Received in revised form 21 April 2016
Accepted 22 April 2016
Available online 11 May 2016

Keywords:
Maraging stainless steels
Spinodal decomposition
First-principles calculation
Three- dimensional atom probe

ABSTRACT

The effect of Co addition on spinodal decomposition of Cr in a new maraging stainless steel was investigated by three dimensional atom probe (3DAP). The concentration profile of Cr and analysis by maximum likelihood method indicated an increase of spinodal decomposition amplitude of Cr in the Co-alloyed maraging stainless steel. The first-principles calculations showed that the increased Fe-Fe ferromagnetic interaction caused by Co addition might facilitate the formation of Cr-rich clusters in bcc Fe.

The addition of Co in maraging stainless steels could be traced back to 1960's when Pyromet X-12 came on the scene [1]. It is generally believed that Co addition could lower the solid solubility of Ti or Mo in martensite matrix of maraging stainless steels, thus producing an increased volume fraction of Mo or Ti containing precipitates to increase the strength [2,3]. However, it was also proposed that Co would inhibit the dislocation recovery [4] and decrease the sizes of precipitates and martensitic blocks, thus producing a higher secondary hardening [5,6]. Whatever the strengthening mechanism is, it is no doubt that Co addition can lead to an increase in strength of maraging stainless steels.

However, it is still unclear how Co addition influences other properties of maraging stainless steel, e.g., corrosion resistant. Recently, the authors have developed a new Co-alloyed maraging stainless steel, which shows a higher strength compared with that without Co [7]. Specifically, when the Co content is 13 wt.%, the tensile strength of the Co-alloyed steel reaches 1928 MPa. Unfortunately, the corrosion resistance of this steel shows an opposite tendency. For example, the Co-alloyed steel with the highest tensile strength showed the worst corrosion resistance. According to previous researches, the poor corrosion resistance of stainless steels always resulted from the Cr-depletion region occurrence [8–11]. It can be concluded that Co should promote the occurrence of Cr-depletion region, which should be come from the spinodal decomposition that will be discussed later. Within the miscibility gap of the Fe-Cr phase diagram, α-α' phase separation could be accomplished by two different paths namely nucleation and growth (NG) and spinodal decomposition (SD) [12]. Since the phase separation found in this work has been demonstrated to be a spinodal decomposition, the phase separation in other literatures is also named spinodal decomposition although this terminology may not be fully accurate for particular conditions.

For the spinodal decomposition in Fe-Cr alloys, it has firstly become a subject of intensive investigations due to the so-called "475 °C embrittlement" resulted from spinodal decomposition [13–16]. In order to improve the comprehensive properties including corrosion resistance, the Fe-Cr alloys have been alloyed with Mo, Ni, Co, etc. Thus, much work has been performed to discuss the effect of alloying elements on spinodal decomposition [13,14,17–19]. Also, because of its potential application as a construction material for nuclear reactors, the effect of ion irradiation on spinodal decomposition [20] as well as Cr segregation [21,22] was also investigated. In conclusion, much work has been occupied on the description of experiment results and the relevant negative effect, however, the underlying theoretical evidence was seldom investigated [23]. Thus, exploring the functional mechanism of alloying elements (Co in this study) on spinodal decomposition in Fe-Cr alloy is worthwhile.

In this work, the 3DAP technology associated with a maximum likelihood method has been employed to investigate the effect of Co on the spinodal decomposition of Cr in the new Co-alloyed maraging stainless steels. The main reason for the promoted spinodal decomposition of Cr should be due to the Co addition, which was studied based on the first-principles calculations.

The chemical compositions of the experimental steels with 0, 5 and 13 wt.% Co are presented in Table 1. Except for Co, the contents of other

* Corresponding authors.
E-mail addresses: wangw@imr.ac.cn (W. Wang), lcyin@imr.ac.cn (L. Yin).

http://dx.doi.org/10.1016/j.scriptamat.2016.04.033

Table 1
Chemical compositions of the experimental steels.

wt.%	C	Cr	Ni	Co	Mo	Ti	Al	P	S	Fe
0 wt.% Co alloy	0.002	12.31	5.42	0.02	5.08	0.41	0.05	0.003	0.004	76.70
5 wt.% Co alloy	0.003	12.06	5.13	5.05	5.13	0.38	0.05	0.005	0.003	72.49
13 wt.% Co alloy	0.005	12.33	4.55	13.10	5.59	0.41	0.09	0.004	0.002	63.92

alloying elements are the same except for acceptable fluctuation. The experimental steels were firstly melted in a 25 kg vacuum induction furnace and then remelted by vacuum arc melting. The remelted ingot was homogenized at 1523 K and then forged into 25 mm square bars. Specimens for tests and observation were subjected to a solution treatment at 1323 K for 1 h followed by a cryogenic treatment in liquid nitrogen (77 K) for 8 h. Finally, the specimens were aged at 773 K for 0.5, 3, 12, 20, 40 and 100 h, respectively, followed by air cooling.

In order to prepare the tips for the 3DAP investigations, square rods of 0.5 mm × 0.5 mm × 15 mm were cut from the aged bulks, and then were etched to sharp needles by a standard two-step electro-polishing technique [24]. 3DAP experiment was performed in a LEAP™ 3000HR atom probe at a base temperature of 60 K with a pulse fraction ratio of 0.2 and a pulse repetition rate of 200 kHz in ultrahigh vacuum of 10^{-8} Pa. IVAS™ 3.6.2 software was used to perform the atom reconstruction and the data analysis [25]. To quantify the spinodal decomposition evolution as a function of aging time, a maximum likelihood method [26] was applied based on the concentration profile of Cr. The spinodal decomposition amplitude was finally calculated by computed iteration.

Fig. 1 presents 3DAP elemental maps of Cr atoms within analyzed volumes of 30 × 30 × 60 nm^3 in all steels aged at 773 K for different times. It can be seen that Cr atoms distributed homogeneously in all steels after cryogenic treatment (Fig. 1a,c,e). However, heterogeneous distribution of Cr atoms can be observed with increasing aging time except for the 0 wt.% Co specimen. Fig. 1a and b show the 3DAP elemental maps of Cr atoms in the 0 wt.% Co specimen, and it can be seen from the two figures that the Cr atoms always distributed randomly even after aging for 100 h. As for the 5 wt.% Co specimen, the decomposition microstructure is observed in the specimen aged for 100 h, as shown in Fig. 1d. However, when the Co content is increased to 13 wt.%, clustering of Cr atoms occurred after aging for 0.5 h, as seen in Fig. 1f. In particular, when the aging time is prolonged to 3 h and 100 h, the decomposition microstructure consisting of Cr-rich zones and Cr-depleted zones can be easily identified, as shown in Fig. 1g and h.

The 3D reconstruction provides a good representation of the space distribution of the Cr atoms, however, the results can't unequivocally demonstrate the expected trends of spinodal decomposition. As an illustration, concentration profiles and related concentration frequency distributions of Cr atoms in the three aged steels were calculated. Then, a maximum likelihood method was used to calculate the spinodal decomposition amplitude of Cr atoms based on the Cr concentration profiles.

Fig. 2a and b show the corrosion current density and spinodal decomposition amplitude calculated by maximum likelihood method as a function of aging time in the three steels, respectively. It can be seen from Fig. 2 that the corrosion current density and spinodal

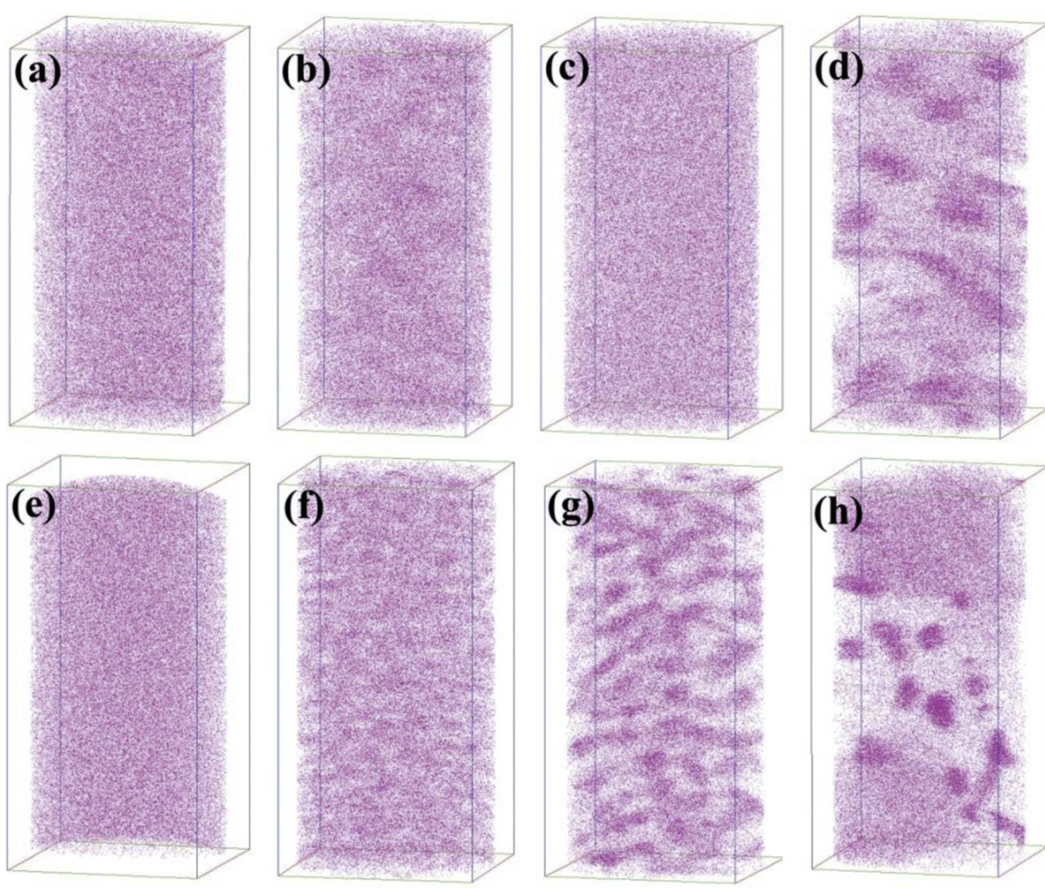

Fig. 1. 3DAP chromium atoms mapping of three alloy specimens aged at 773 K for different times. All the analyzed volumes are with the dimensions of 30 × 30 × 60 nm^3. (a), (c) and (e) are specimens after cryogenic treatment in 0 wt.% Co, 5 wt.% Co and 13 wt.% Co alloys; (b) and (d) are specimens after aging for 100 h in 0 wt.% Co, 5 wt.% Co alloys; (f), (g) and (h) are specimens after aging for 0.5 h, 3 h and 100 h respectively in 13 wt.% Co alloy.