Materials Science and Engineering A 534 (2012) 552–556

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering A

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

A phase-field and electron microscopy study of phase separation in Fe–Cr alloys

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ARTICLE INFO

Article history:
Received 10 October 2011
Received in revised form
29 November 2011
Accepted 2 December 2011
Available online 13 December 2011

Keywords:
Phase transformation
Steel
Electron microscopy
Spinodal decomposition
Hardening
Phase-field modeling

ABSTRACT

Phase separation in the binary Fe–Cr system, the basis for the entire stainless steel family, is considered responsible for the low temperature embrittlement in ferritic, martensitic and duplex stainless steels. These steels are often used in load-bearing applications with considerable service time at elevated temperature. Thus, understanding the effect of microstructure on mechanical properties and predicting dynamics of phase separation are key issues. In the present work, experimental evaluation of structure and mechanical properties in binary Fe–Cr alloys as well as phase-field modeling, using a new thermodynamic description of Fe–Cr, is conducted. A significant hardening evolution with time is found for alloys aged between 400 and 550 °C, and it can be attributed to phase separation. The decomposed structure changed with increasing Cr content at 500 °C, with a more particle-like structure at 25 wt% Cr and a more spinodal-like structure at 30 wt% Cr. The observed transition of structure agrees with the thermodynamically predicted spinodal, although the transition is expected to be gradual. The phase-field simulations qualitatively agree with experiments. However, to enable accurate quantitative predictions, the diffusional mobilities must be evaluated further and thermal fluctuations as well as 3D diffusion fields must be properly accounted for.

1. Introduction

In systems with a miscibility gap, a special type of phase transformation is found where the atoms only redistribute on the old lattice sites without any change in the crystal structure. There is a tendency for the system to phase separate inside the miscibility gap and it is possible to define a spinodal from equilibrium thermodynamics. The spinodal acts as a limit of instability [1], but the prediction of the spinodal has been questioned [2]. It is still unclear whether the energy barrier for nucleation goes to zero at the spinodal and/or if the crossing of the spinodal is significant for the phase separation kinetics. Moreover, the difference in microstructure between the metastable and unstable region in the phase diagram is debated.

A system of great technical importance, which displays a miscibility gap at low temperatures is Fe–Cr. The phase separation of ferrite into Fe-rich (α) and Cr-rich (α') areas leads to an increased hardness and strength but decreased ductility and impact toughness, which is historically referred to as the 475 °C embrittlement [3]. The Fe–Cr system is well investigated, but in recent time there is a renewed interest, much due to the potential use of new Fe–Cr alloys in nuclear technology applications [4]. In these applications, the steel will be subjected to load and should be capable of withstanding thermal aging for decades without suffering embrittlement. Such embrittlement could have large consequences and hence it is crucial to understand the effect of microstructural evolution on mechanical properties. In addition, physical modeling and accurate predictions of phase separation dynamics would enable long-term life time assessments, which is not practically within reach from experimental information.

Despite all the work on Fe–Cr, it is still not possible to predict the phase separation kinetics using physical modeling due to insufficient modeling strategies as well as lack of reliable thermodynamic [5] and kinetic data. In addition, it is difficult to accurately visualize the microstructural evolution in the Fe–Cr system using electron microscopy, due to the low misfit between Fe and Cr. Some previous transmission electron microscopy (TEM) investigations are therefore misleading. Today, the atom probe provides a good complementary tool to TEM and in the light of several atom probe studies on Fe–Cr it seems justified to make a comparison with TEM.

In the present work, a new thermodynamic description of Fe–Cr [6] is used as input to kinetic modeling using a phase-field approach. In addition, the evolution of mechanical properties is assessed using micro-hardness measurements and the microstructure is investigated using TEM. The coupling of theoretical and experimental investigations provides new knowledge on the assessment techniques for this system. Moreover, it generates insights on the phase separation dynamics in the Fe–Cr system and the effect of microstructure on mechanical properties.

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doi:10.1016/j.msea.2011.12.007

2. Methodology

2.1. Experimental procedure

Ten experimental casts of Fe–Cr with Cr contents ranging from about 10–55 wt% were produced (Table 1).

Prior to any further treatments, all samples were homogenized at 1100 °C for 2 h, except for 10 wt% Cr which was homogenized at 700 °C for 20 h, in inert argon atmosphere. After homogenization, the samples were quenched in brine followed by isothermal aging at temperatures from 400 to 600 °C using different times. The isothermal treatments were conducted in air atmosphere and before further investigations the thin oxide scale was removed. The unaffected average chemical composition was verified using atom probe tomography (APT) and energy dispersive X-ray spectroscopy (EDS) in the scanning electron microscope (SEM).

Samples for micro-hardness measurements were prepared by grinding and polishing. Three micro-Vickers hardness measurements per sample using 100 g load were performed.

Thin foils were prepared by sectioning 400 μm slices and polishing on both sides to the thickness of 100 μm. 3 mm discs were punched out and subsequently, electron transparency was achieved by electro-polishing in an electrolyte consisting of 15% perchloric acid and 85% methanol at −18 °C and 20 V. The microstructure was observed using a JEOL 2000FX TEM operating at 200 kV.

2.2. Phase-field modeling

The microstructure evolution was modeled with a modified diffusion equation

$$\frac{1}{V_m}\frac{\partial x_{Cr}}{\partial t} = -\nabla \cdot J_{Cr} \tag{1}$$

where x_{Cr} is the mole fraction of chromium and V_m is the molar volume. The flux of chromium is given by

$$J_{Cr} = -L_{CrCr}\nabla\frac{\delta G}{\delta x_{Cr}} \tag{2}$$

L_{CrCr} is a phenomenological coefficient related to the diffusional mobilities of Cr and Fe [7]. The total Gibbs energy is given by [8]

$$G = \frac{1}{V_m}\int \{G_m(x_{Cr}, T) + \frac{1}{2}\varepsilon^2(\nabla x_{Cr})^2\} d\Omega \tag{3}$$

where the integral in (3) is taken over the volume (Ω) of interest, G_m is the molar Gibbs energy taken from the new thermodynamic description [6]. Eq. (3) in (2) and combined with (1) is usually called the Cahn–Hilliard equation [1]. The ε^2 is the so-called gradient energy coefficient here taken to be [8]:

$$\varepsilon^2 = \frac{\omega_{CrFe}\delta^2}{2} \tag{4}$$

where ω_{CrFe} is the regular solution parameter and δ^2 is the interatomic distance. For simplicity, in this work it is assumed that L_{CrCr} is independent of composition but dependent on temperature. This will make Eq. (1) less non-linear and easier to solve. Eq. (1) is solved in 1D using the finite volume PDE solver, FiPy [9]. In order to be able to update G_m at each time step FiPy was coupled to Thermo-Calc [10] through a newly developed python interface [11]. The diffusional mobilities were taken from the kinetic database MOB2 [12].

3. Results and discussion

The evolution of micro-hardness at 500 °C for all ten experimental alloys is displayed in Fig. 1a. It has previously been found

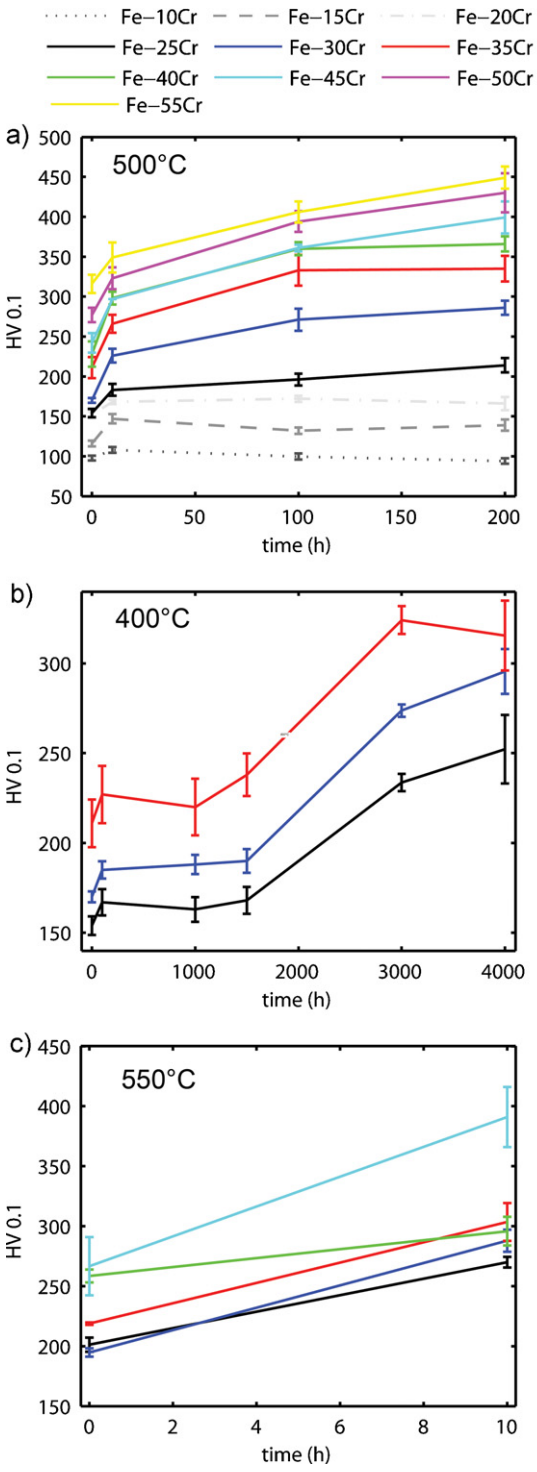

Fig. 1. Micro-hardness of samples aged for different times at (a) 500 °C, (b) 400 °C and (c) 550 °C.

that the micro-hardness is sensitive to rather small changes in phase separation [6], and in Fig. 1a, the micro-hardness increases rather rapidly with time and this is more pronounced for alloy compositions well inside the miscibility gap. This is probably due to the increased driving force for decomposition with increased Cr content, which leads to faster kinetics. The more substantial decomposition generates higher internal stresses between Fe-rich and Cr-rich domains and thus generates an enhanced strengthening effect [13]. The indications from previous atom probe work is that the spinodal is located at about 25–30 wt% Cr at 500 °C [6,14]