Phase Transformation Behavior and Microstructural Control of High-Cr Martensitic/Ferritic Heat-resistant Steels for Power and Nuclear Plants: A Review

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The martensitic/ferritic steels have been used as boiler and turbine materials in power plants, and also been selected as potential materials for structural materials in nuclear reactors. In this paper, the kinetic analysis of the martensite formation and microstructural control of high-Cr martensitic/ferritic steels are reviewed. A modular approach, incorporating Fisher partitioning nucleation and anisotropic growth for impingement, was proposed to describe the martensite formation kinetics under different cooling rates. The kinetic analysis suggested a thermal-activated growth feature occurring during the martensitic transformation of martensitic steels. The microstructure can be tuned by composition optimization and various combinations of heat treatment parameters (temperature, time, severe and minor deformation). For the application in power plant, the potential of boundary-design, refinement of original austenite grain size and the final martensite lath, pinning effect of stable carbides, in improving the performances of martensitic/ferritic steels at elevated temperatures should be investigated more thoroughly. Furthermore, efforts should be made to explore the effects of retained austenite on the improvement of high-temperature creep strength. For the application of nuclear plants, attempts should also be made to produce Fe powders with uniformly distributed oxide particles by chemical reactions.

1. Introduction

The high-chromium (9–12 wt%) martensitic heat-resistant steels were developed during the first half of the last century, and for a long time have been used as boiler and turbine materials in power-generation plants[1,2]. In the 1970s, the 9–12 wt% Cr–Mo steels were first taken into consideration for elevated temperature in-core application (cladding, wrappers and ducts) for fast fission reactors, and the structural materials for the first wall and blanket structures of fusion reactors, due to their advantages in swelling resistance and thermal properties over austenitic stainless steels[3–6].

By adding Mo, V, Nb to simple Cr–Mo steels, optimizing the contents of C, N, V and Nb, partially replacing Mo by W, adding elements Cu, N, B, and increasing the percentage of W, adding the element Co, the maximum use temperature of martensitic steels for power plants has been increased dramatically[3]. With respect to the martensitic steels for nuclear reactors, which are generally developed out of the martensitic steels for power plants, minor changes in the composition will be made, in order to meet the requirement for the radiation resistance in fusion programs[7–11].

The microstructures of martensitic steels are generally characterized by the tempered martensite decorated with precipitates (mainly $M_{23}C_6$ carbide and MX carbonitride)[2]. At elevated temperatures, the coarsening rate of $M_{23}C_6$ will be accelerated, and the more stable MX can contribute to the Z phase formation, deteriorating creep strength. Therefore, the oxide nanoparticles with unparalleled thermal stability are introduced into the martensitic steels, aimed at increasing the upper temperature limit while maintaining the advantages inherent in martensitic steels, leading to the study and development of oxide dispersion strengthened (ODS) martensitic/ferritic steels[12,13].

As mentioned above, the development of martensitic/ferritic steels is always promoted by composition adjustment. And currently, attention is frequently paid on the microstructure evolution involved in martensitic/ferritic steels[14–17]. Intentional

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microstructural control of martensitic/ferritic steels through heat treatment processes is less reported. Thus in this paper, we review and discuss the strategies to obtain some specific microstructures in these steels. The kinetic analysis of martensite transformation, which plays a significant role in the final microstructure of martensitic steels, will also be discussed.

2. Kinetic Analysis of the Martensite Formation in High-Cr Martensitic Steels

The transformation kinetics is dependent on the simultaneous nucleation and growth processes of the product phase, and extensive work has been carried out on the determination of the kinetic mechanisms from the past overall kinetics studies. Among them, a general procedure to determine the analytical phase transformation model on the basis of nucleation, growth and impingement mechanisms has been proposed[18–20], as indicated in Fig. 1. More details can be found in Ref. [20]. This general procedure has been successfully applied to the massive austenite-ferrite phase transformations of Fe-based alloys[21–23], as well as the crystallization process of amorphous alloy[24–26].

Although the martensitic transformation in steels has received considerable attention over the years, owing to its widespread applications, more emphasis was focused on the onset of transformation and crystallographic orientation relationship between the austenite and martensite, instead of the kinetic description of the very fast martensite transformation (10^{-4}–10^2 m s^{-1}[27]) as a function of cooling rate. For example, the classic Koistenen and Marburger equation[28]:

$$f = 1 - \exp[\beta(M_S - T)]$$

where f is the martensite fraction, M_S denotes martensite start temperature, T denotes the temperature, β is a constant approximately equal to -0.011/K($^\circ$C)[29], which cannot be used to describe the progress of transformation under different cooling rates.

Very recently, a modular phase-transformation model, incorporating the classic partitioning analysis for nucleation and anisotropic growth for impingement, has been developed to extract the velocity of the migrating martensite/austenite interface from the dilatometric data. The obtained velocity of the martensite/austenite interface as function of temperature indicates a thermally-activated growth governed by relatively low activation energy, as determined by evaluation of the martensite-formation-rate maximum as a function of cooling rate. For more details on the construction of the
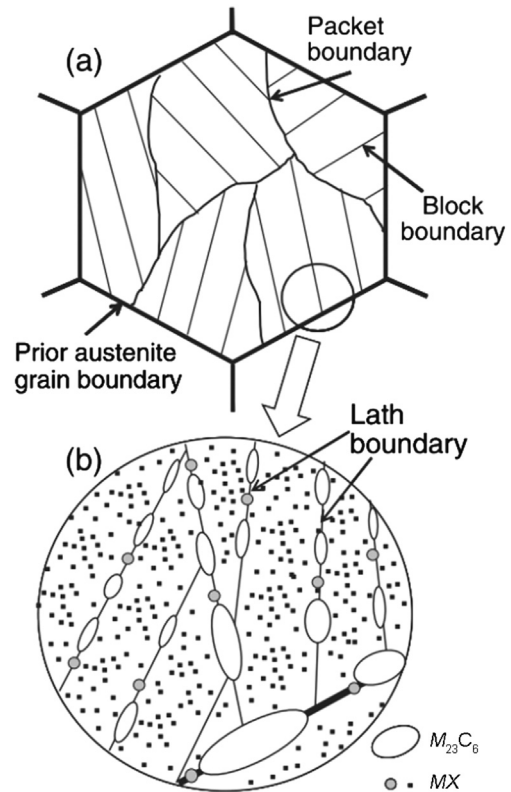

Fig. 2. Schematic representation for the microstructure of 9%–12% Cr steels after tempering[2].

analytical phase transformation model, please see Ref. [30]. This new attempt has been used for the kinetic analysis of the high-Cr ferritic heat-resistant steel[31], and the calculated interface migration velocities are characterized by a relatively low value ($\sim 10^{-5}$ m s^{-1}), which also suggests a thermally-activated martensitic growth feature.

3. Microstructure Modifications of Martensitic/Ferritic Steels

Martensitic/ferritic heat-resistant steels can be strengthened through solute hardening, dispersion hardening, dislocation hardening and sub-boundary hardening[2]. The 9−12 wt% Cr martensitic
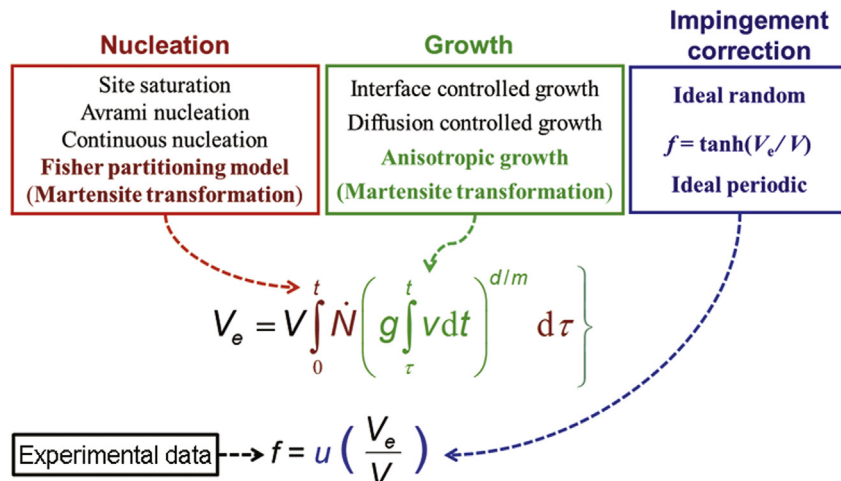

Fig. 1. Schematical diagram illustrating the nucleation, growth, and impingement correction modes when a modular analytical phase transformation was developed; see Ref. [20].