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# Precipitation of Laves phase in eutectoid type reaction: δ-Fe → γ-Fe + Laves in Fe-Cr based ferrous alloys

Zhetao Yuan

This thesis focuses on understanding the precipitation kinetics and morphologies on the eutectoid type reaction pathway: δ-Fe → γ-Fe + $Fe_2M$ (Laves) which appears in the Fe-Cr-M (M includes Hf and Ta) ternary systems, with a final goal to develop a new heat resistant ferritic steels strengthened by the Laves phase precipitates with better temperature capability and longer durability for high-temperature components of high efficiency steam turbine powerplants. Phase equilibria among the δ, γ, and $Fe_2M$ phases are quantitatively investigated to design experiments where the supersaturation for a δ→γ phase transformation and that for the precipitation of the Laves phases were controlled independently to study the dominant factors in the kinetics of the phase transformation and precipitation morphology. A principle to achieve a fine dispersion of Laves phase and a better microstructural controllability is proposed based on this study. This thesis consists of 6 chapters, and the main results obtained in each chapter are summarized as follows:

**Chapter 1: General Introduction.** The history, the status, and future demands for thermal power plants are briefly overviewed, and a necessity to continue improve the temperature capability/durability of heat resistant steels for the powerplant applications is explained. The reasons to focus on Laves phase as a strengthener for the heat resistant ferritic steels and the previous research where a new strengthening strategy using interphase precipitation which occurs on the eutectoid type reaction pathway: δ-Fe→γ-Fe+$Fe_2M$ are outlined. A limited understanding of the precipitation kinetics and morphology along the eutectoid reaction path and a poor controllability for the interphase precipitation are subsequently explained. Finally, the objectives, and structure of this thesis are introduced.

**Chapter 2: Phase Equilibria in the Fe-Cr-M (M: Hf, Ta) Ternary Systems.** Phase equilibria among the δ, γ, and $Fe_2M$ phases have been determined in the Fe-Cr-M (M: Hf, Ta) ternary systems using bulk alloys heat-treated at high temperatures. The thermodynamic database was been modified to reflects reported binary phase diagrams and the experimental phase diagrams determined in the present study. The thermodynamic calculation suggests that the supersaturation of Hf/Ta for the formation of γ phase is higher in the Hf doped system than in the Ta doped system. The supersaturation for the Laves phase formed from δ phase is barely depended on Cr contents. The knowledges obtained in this chapter were used in designing the experiments in chapters 3 and 4.

**Chapter 3: Effect of γ growth rate on the competition of the precipitation modes: interphase precipitation vs. fibrous precipitation.** Effects of the Cr content on the precipitation kinetics and resulting morphologies of the $Fe_2Ta$ precipitates along the eutectoid reaction path: $\delta \rightarrow \gamma + Fe_2Ta$ have been investigated to understand the criteria to distinguish the two eutectoid reaction modes: interphase precipitation (IPP) and fibrous precipitation (FP). The γ growth follows a linear relationship with time, which suggests that the γ phase grows by the ledge mechanism. A reduction of the Cr content was found to accelerate the γ growth rate and change the reaction mode from FP to IPP accordingly. A further reduction prevented the precipitation of the $Fe_2Ta$ phase. A competition between the growth of γ phase through the ledge mechanism and the growth of needle shaped Laves phase precipitate was to interpret the competition between the two reaction modes.

**Chapter 4: Effects of Laves phase forming element on the nucleation of interphase precipitation.** Effects of alloying elements on the nucleation rate of Laves phase on moving δ/γ interface was investigated by evaluating the critical γ growth rate and critical time for IPP. The critical γ growth rate was estimated as about 150μm/s in Hf doped alloys and 5~8μm/s in Ta doped alloys. The nucleation time given for IPP, evaluated as a time between arrivals of two chasing interphase ledges, was calculated to be less than ~1 ms in Hf doped alloys and about few tens of milliseconds in Ta doped alloys. The different nucleation time between the alloys can be interpreted by much higher driving force for Laves phase precipitation in Hf doped alloys than in Ta doped alloys.

**Chapter 5: Improvement in heat treatability to achieve a fine dispersion of Laves phase through interphase precipitation.** Effects of alloying elements on the direct precipitation of Laves phase in the δ phase (DP) were investigated. The nucleation rate of DP was found to be 2~3 orders of magnitude faster in Hf doped alloy than in Ta doped alloys. The heat treatment window to induce IPP, between the onset of IPP and DP, is ~10s at 1050°C~1100°C in Hf doped alloys and ~60s at around 950°C in Ta doped alloys. A relatively slow IPP nucleation rate and a wider heat treatment window for IPP in Ta doped alloys allow us to form a fine dispersion of Laves phase regardless of the size of material as far as the δ grain size is smaller than 500μm.

**Chapter 6: General Summary.** The main results obtained in each chapter are summarized.