

The design of a compositionally robust martensitic creep-resistant steel with an optimized combination of precipitation hardening and solid-solution strengthening for high-temperature use

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Abstract

Precipitation hardening and solid-solution strengthening (SSS) are the most effective strengthening mechanisms in creep-resistant, corrosion-resistant ferritic/martensitic steels. However, it is difficult to achieve a simultaneous maximization of both mechanisms as alloying elements may affect both mechanisms in a different way and upset considerations based on one strengthening mechanism only. To address this challenge, a generic alloy-by-design model was developed. The model uses quantitative descriptions for both the time-dependent precipitate population and its resulting strengthening contribution and the time-independent SSS due to chemical elements remaining in solid solution. Furthermore, the model involves full thermodynamic calculations at appropriate temperatures. The formulations were found to capture the contributions of both strengthening mechanisms in existing Cr containing martensitic steel grades rather precisely. Subsequently, the model was used to probe new steel compositions in the compositional domain of 9–12% Cr martensitic creep-resistant steels containing nine other alloying elements, each at different concentration levels. A genetic algorithm was used to probe the compositional search domain. The calculations were performed assuming a continuous operating temperature of 650 °C and a lifetime of at least 10⁵ h. Alloy compositions and heat treatment conditions leading to too large amounts of undesirable phases and other detrimental effects were automatically rejected. A Pareto front linking the strength contributions according to precipitation hardening or SSS was constructed by combining results of two separate optimization routes. From the Pareto front analysis, steel compositions with optimized combinations of strengthening mechanisms were identified. The robustness of the new solutions was tested by enforcing concentration variations as encountered in industrial practice and to test for abrupt changes in predicted creep strength values. The newly designed steel is predicted to significantly outperform existing commercial creep-resistant martensitic steel grades and has a target composition such that the usual deviations in elemental concentration levels do not significantly affect the final creep strength. © 2014 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Alloy design; Solid solution strengthening; Precipitation hardening; Creep; Composition

1. Introduction

Martensitic/ferritic 9–12% Cr steels are widely applied in boiler and turbine components in coal-fired ultra-supercritical power plants owing to their good performance at operating temperatures up to 600 °C [1]. Nevertheless, a

higher operating temperature, such as 650 °C, would be desirable to increase the efficiency of electricity generation and to decrease the CO₂ emission. However, the microstructural stability of existing creep steel grades during long term exposure at elevated temperatures is still insufficient. Much effort has been devoted to the development of new martensitic creep-resistant steel with improved creep strength and a decent stability during long term service [2–11].

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Kimura et al.'s research [12,13] on some ferritic creep-resistant steels has shown that at very long times the creep strength reaches a constant value. This inherent strength was taken to be due to the matrix solid-solution strengthening (SSS) only as all precipitation hardening (PH) contributions had disappeared because of coarsening [13]. For very long service times and high use temperatures, other strengthening mechanisms such as work hardening and lath size strengthening can also be ignored [13]. Hence an ideal creep-resistant steel has a matrix with a high degree of SSS and contains a high volume fraction of precipitates with an extremely slow coarsening rate. Furthermore, such an ideal steel should have a microstructure free of undesirable phases.

Nano-sized MX (M: metallic elements; X: C and N) carbonitrides are known to have a very slow coarsening rate and their formation and coarsening rates were shown to explain the creep behaviour of 9–10 wt.% Cr ferritic steels as a function of temperature and time [14]. The optimal PH effect is achieved mainly by tuning the precipitate forming elements and their concentrations. For example, experimental results have shown that different combinations of MX carbonitride formers, i.e. C, N, Nb, V and Ti, determine the precipitation size, volume fraction, coarsening rate and distribution of precipitates, etc., which ultimately determine the microstructural stability and time-dependent creep strength [3,7,11,15]. However, computational investigations suggest that the coarsening rate of MX carbonitrides could be 1000 times lower by tuning all alloying elements, also those remaining in solid solution in the matrix, simultaneously [16,17]. Other precipitates, such as $M_{23}C_6$ carbides [4], Z phase [18] and Laves phase [19,20] display similar strengthening effects. The initial precipitate size and coarsening rate of $M_{23}C_6$ carbides are much bigger and higher than those of MX carbonitrides [21], although the addition of B and Co has been reported to moderately decrease their coarsening rate [22–24]. The Z phase and Laves phase generally precipitate only after long term exposure, and are traditionally considered as detrimental phases in creep-resistant steels. However, their formation can be accelerated by tuning the levels of Z or Laves phase forming elements [25], such as Cr and Nb, and adjusting the heat treatment parameters. Moreover, such precipitates display more desirable morphologies and distributions, and thus strengthen the materials [18–20]. While PH clearly is an effective way to increase the creep strength of steels, the unavoidable precipitate coarsening process invariably leads to a lowering of the creep strength with time and temperature. In contrast, SSS depends on temperature but is essentially time-independent. W and Mo are the common elements to increase the solid-solution strength of martensitic creep-resistant steels [26,27]. The addition of 2.3 wt.% W in a α iron solution with 0.001 wt.% C can decrease the creep strain rate by a factor of 100 or more [26]. However, the W and Mo concentrations present in the matrix at an early stage drop considerably due to the precipitation of W and Mo enriched Laves phase after a long term exposure

at high temperatures [28]. Recently Al, Ni, Mn and Si have been proposed as more stable elements to improve the strength of ferritic matrix for long term applications [29]. Some early research has been done to quantify the contributions of PH and SSS separately and then to calculate their combined effects on alloy strength [30,31]. However, such an approach does not automatically lead to optimal results as the effect of individual chemical elements on the final creep strength is far from simple because of many complex interactions between different alloying elements and the resulting influences on the two principal strengthening mechanisms, PH and SSS. For example: (i) additions of elements contributing to SSS could thermodynamically and kinetically influence the volume fraction, size and coarsening rate of desirable precipitates; (ii) additions of elements contributing directly or indirectly to PH could change the solubility of all elements in the matrix and hence the SSS; (iii) additions of either PH or SSS elements could change the entire thermodynamics and may promote the formation of undesirable microstructural components. Finally, the sum of all alloying elements may be such that neither a fully austenitic homogenization state nor a fully martensitic state upon quenching can be obtained.

Clearly, simultaneously maximizing these two strengthening mechanisms in a complex multi-component 9–12% Cr martensitic steels system by a priori tuning the concentration of each element concentration and ascertaining a fully martensitic microstructure with a resulting fine grain size and high precipitation density remains an unsolved scientific challenge. The coupled thermodynamic/genetic algorithm design concept to be presented identifies the composition of a martensitic creep-resistant steel grade ideally suited for long term application at a target temperature of 650 °C. The steel has an optimal combination of significant PH due to slowly coarsening MX carbonitrides and a high degree of SSS. The defined composition does not lead to the formation of undesirable phase fractions and results in a steel with a fully martensitic microstructure. However, with such an ideal composition defined it may not be possible to actually produce such a steel, as in industrial practice it is impossible to reach the exact concentration level for each of the alloying elements simultaneously. Small compositional deviations may lead to large changes in microstructure and creep behaviour. To account for this, the model is modified such that for the finally advised steel composition the intended creep properties are also maintained if the actual steel composition deviates within the usual industrial margins from the target composition.

2. Methodology

2.1. Design methodology

The design methodology used follows the “alloy by design” approach presented elsewhere [32]. Two key conversions form the basis of this method, as shown in the upper part of Fig. 1: the “translator”, which associates

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