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Designing high-temperature steels *via* surface science and thermodynamics

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ABSTRACT

Electricity in many countries such as the US and China is produced by burning fossil fuels in steam-turbine-driven power plants. The efficiency of these power plants can be improved by increasing the operating temperature of the steam generator. In this work, we adopted a combined surface science and computational thermodynamics approach to the design of high-temperature, corrosion-resistant steels for this application. The result is a low-carbon ferritic steel with nanosized transition metal monocarbide precipitates that are thermally stable, as verified by atom probe tomography. High-temperature Vickers hardness measurements demonstrated that these steels maintain their strength for extended periods at 700 °C. We hypothesize that the improved strength of these steels is derived from the semi-coherent interfaces of these thermally stable, nanosized precipitates exerting drag forces on impinging dislocations, thus maintaining strength at elevated temperatures.

1. Introduction

In the US, about 67% of the generated electricity is produced by burning fossil fuels, of which coal contributes about 39% [1]. The corresponding numbers for China are 69% and 63% [2]. Burning of coal not only emits more carbon dioxide per kWh electricity produced compared with natural gas [3], but also particulates and other toxic pollutants such as mercury and arsenic [4]. Since it is unlikely for the US, China and other countries to stop burning fossil fuels to produce electricity in the foreseeable future, the most reasonable solution to mitigate CO_2 and pollutant emission is to make power plants more efficient. US coal-fired power plants operate at an average efficiency of 32%, emitting about 1000 gm CO_2 per kWh electricity produced. According to the World Coal Association, if one can raise the efficiency to 50%, the CO_2 emission will be reduced to about 700 gm per kWh [5].

One can increase the thermal efficiency of these power plants by operating the steam generator at higher temperatures (and pressures). Most steam turbines in the US operate at 540 °C or below, and the proposed target by the US Department of Energy is to increase the operating temperature to 760 °C. Extensive research studies are being conducted on the use of Ni-based superalloys for such applications, and results are quite promising [6]. The only drawback is the cost of the superalloys, about $30–40/kg in 2015. An alternative is to explore the use of high-performance steels in steam generators that can maintain 35 MPa strength for 100,000 h at 600 to 625 °C. In this initial study, we will focus on meeting the 600 °C temperature goal through accelerated aging tests at 700 °C.

Strength of structural steels is normally achieved by four methods: solid solution strengthening, strain hardening, grain refinement, and precipitates [7]. For the purpose of this discussion, let us focus on precipitates, which act as obstacles against dislocation motion, thus providing strength to the steel. Precipitate strengthening scales roughly as the inverse of the spacing between these precipitates. Extended operation at elevated temperatures results in coarsening of these precipitates (Ostwald ripening) and hence increased spacing between precipitates [8]. Therefore, the first-order solution to having steels with adequate strength for extended high-temperature operations is to incorporate thermally stable precipitates in steels.

2. Design approach

2.1. Precipitate structure

In the early stage of precipitate growth and assuming interfacial kinetics controlled growth, the growth velocity v of a precipitate due to arrival of solute atoms from the matrix to the precipitate surface is given by [9]:

$$v \propto \exp(-\Delta f_m/kT)\left[1-\exp\left(-\Delta f_{mp}/kT\right)\right]$$

where Δf_m is the activation energy for the migration of the solute atom from the matrix to the precipitate, Δf_{mp} is the free energy difference between the solute atom in the matrix and precipitate, k is the Boltzmann

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constant, and T is temperature. Δf_{mp} contains an interfacial energy term; the sign of Δf_{mp} is such that a coherent matrix–precipitate interface makes Δf_{mp} more positive, resulting in a higher growth rate. This implies that just nucleated precipitates should be coherent with the matrix. Upon further aging, precipitates coarsen through an Ostwald ripening process, i.e., larger precipitates growing at the expense of smaller ones. This process is described well by the LSW equation [10], i.e.,

$$R(t)^3 - R_o^3 \propto \gamma D(t - t_o)$$

where $R(t)$ is the precipitate radius at time t, R_o is the precipitate radius at t_o, D is the diffusivity of the solute atom, and γ is the interfacial free energy. This equation indicates that coherent precipitates with low interfacial free energy and made of slow diffusing elements will grow slower than incoherent ones.

One suitable candidate for such precipitates is NiAl, which has a B2 (CsCl) structure with a lattice constant of 0.289 nm. This is virtually identical to that of *bcc* Fe (0.287 nm). Indeed, NiAl is being studied as a viable precipitate for high-temperature steels [11]. Another candidate is MC, transition metal monocarbide with the B1 (NaCl) structure, VC and NbC being two such examples. Lattice constants of VC and NbC are 0.417 [12] and 0.447 nm [13,14] respectively. These carbide precipitates will form with a Baker–Nutting orientation on the *bcc* iron lattice [15,16]. The length of the unit vector along the [110] direction of *bcc* Fe is $0.287 \times 2^{1/2} = 0.406$ nm. Therefore, on the (001) plane, MC is coherent with Fe (45° rotation) with lattice mismatch of 2.7% for VC and 10.1% for NbC. Along the [010] direction, MC is commensurate with Fe (two unit cells of MC matching three unit cells of Fe) with lattice mismatch of 3.3% for VC and 10.1% for NbC. Therefore, in order for the MC precipitate to form coherent interfaces with the Fe matrix to achieve low interfacial energy, the system has to pay a strain energy penalty. Minimization of the total free energy results in the MC precipitate forming a coherent or semi-coherent interface, as shown in Fig. 1.

The semi-coherent interface formed between MC precipitates and the Fe matrix is not necessarily a disadvantage. At elevated temperatures, precipitates become less effective obstacles against dislocation climb due to thermal activation. However, it has been shown [17–19] that a semi-coherent precipitate–matrix interface has an attractive interaction with an impinging dislocation. Fig. 2 shows a dislocation bypassing a spherical precipitate as it sweeps over its surface. As the dislocation sweeps over the precipitate, the attractive interaction by the semi-coherent precipitate–matrix interface exerts a drag on the dislocation, reducing its mobility and maintaining the alloy strength even at elevated temperatures.

2.2. Computational thermodynamics modeling

In addition to Fe, plain carbon steels contain C, Si, and Mn, the latter two elements added for the purpose of deoxidation and scavenging of residual sulfur respectively [20]. In this work, four additional alloying elements will be considered: Cr for corrosion protection, Mo for slower diffusion, Nb and V for the formation of MC precipitates. We used computational thermodynamics to select the appropriate steel composition with the objective to maximize the phase fraction of MC, especially at elevated temperatures. Commercial software (Thermo-Calc) was used with the SGTE Solutions Database version 2.1 (SSOL2). The Scientific Group Thermodata Europe developed the SGTE/SSOL2 database. For simplicity, we will present only the weight percentage of Cr and V. An example of one such computation for a low-carbon steel is illustrated in Fig. 3(a), which shows a vanadium isopleth for steel composition containing 10Cr–xV (in wt. %). When the V concentration is greater than or equal to 1.0 wt. %, MC is the only stable precipitate phase between 600 and 800 °C. More important, the equilibrium concentration of complex carbide $M_{23}C_6$ steadily decreases with increasing V concentration, while the MC phase fraction increases, as shown in Fig. 3(b) and 3(c). At sufficiently high V concentration, the $M_{23}C_6$ carbide phase disappears above a certain temperature. $M_{23}C_6$ is not a desirable phase because it is not stable against coarsening at elevated temperatures, so we seek to minimize the amount present in our alloys.

Fig. 3(a) also shows that over the range of vanadium composition shown, the $M_{23}C_6$ phase is completely dissolved above 800 °C. Sufficiently rapid cooling may suppress the formation of this undesirable carbide during the manufacturing process.

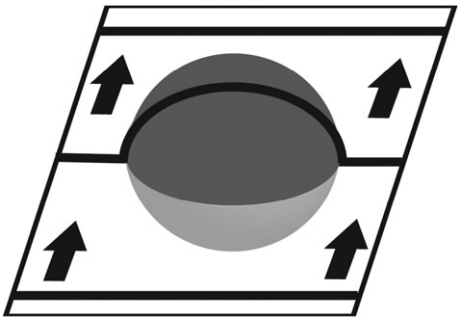

Fig. 2. Depiction of a line dislocation bypassing a spherical precipitate.

3. Experimental methods

Fabrication of the experimental steels was done through vacuum arc melting of 11 g ingots with the desired composition. Each ingot was inverted 4 times during melting to ensure homogeneity throughout the sample. All samples were normalized for 1 h at 975 °C after arc melting and then air-cooled. Microstructures of selected samples were observed using an optical microscope before and after aging treatment at elevated temperatures. Samples were ground flat using carbide grinding paper, and final polishing was done with 1 μm diamond suspension. Samples were then etched using a 2% nital solution to reveal grain boundaries.

Mechanical properties were evaluated using Vickers indentation at 700 °C in partial vacuum (pressure < 20 Pa). The applied load was

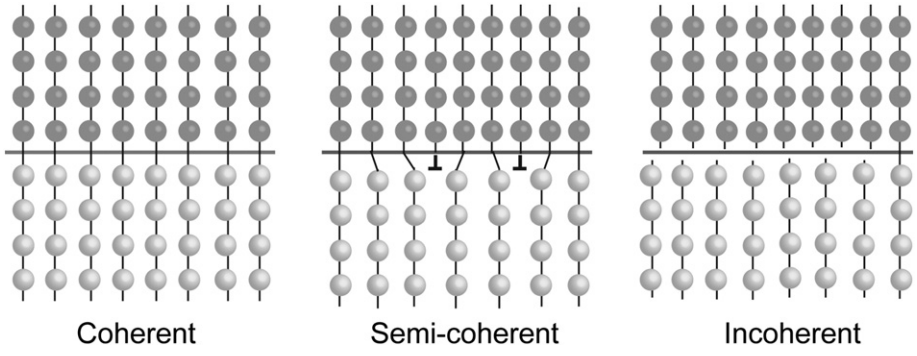

Fig. 1. Schematic examples of different interface types.