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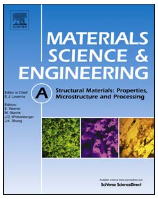

Atomic resolution characterization of strengthening nanoparticles in a new high-temperature-capable 43Fe-25Ni-22.5Cr austenitic stainless steel

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ABSTRACT

Advanced scanning transmission electron microscopy (STEM) was used to study two distinct populations of nanoparticles associated with the extraordinary strengthening of the highly-alloyed austenitic stainless steel Sanicro 25 during cyclic loading at 700 °C. Fully coherent and homogeneously dispersed Cu-rich nanoparticles precipitate rapidly as a result of thermal exposure, along with nanometer-sized incoherent NbC carbides that nucleate on dislocations during the cyclic loading at high temperature. The atomic structure of nanoparticles was investigated by probe-corrected high-angle annular dark-field STEM imaging. Compositional analysis of the nanoparticles was conducted using high spatial resolution energy dispersive X-ray spectroscopy combined with electron energy-loss spectroscopy. Experimental observations were validated by image simulations of the Moiré-like contrast exhibited by NbC carbides. The important role of both nanoparticle populations for the overall cyclic response is discussed. As a result of pinning effects and associated obstacles, dislocation motion is significantly retarded preventing formation of substructures with lower stored internal energy. With recovery heavily suppressed, forest dislocation strengthening supported by precipitation and solid solution hardening, leads to the remarkable increase of cyclic strength at elevated temperatures.

1. Introduction

Increased demand on the coal-fired power generation industry to improve the efficiency of power plants and thereby reduce emissions led to a need for development of new heat-resistant materials with improved high-temperature strength, enhanced creep properties, and high-temperature corrosion resistance at the proposed increased operating temperatures of 700 °C [1]. Excluding possible candidate materials in the field of Ni-based superalloys, attention was put towards notably more cost-effective heat resistant austenitic steels. One of the alloys newly developed primarily for use in next generation advanced ultra-supercritical (A-USC) coal-fired boilers is the 22.5Cr25NiWCoCuNb austenitic stainless steel designated as Sandvik Sanicro 25.

Compared to other steels in this class (e.g. NF709, Super304H, etc. [1–6]), this alloy has unique composition in terms of type and amount of chemical elements used together. It is based on the Fe-Ni-Cr alloy system with high amount of Ni and Cr combined with a variety of additional alloying elements. While 22.5 wt% Cr should provide good steam oxidation resistance and hot corrosion resistance, a high Ni content of approximately 25.0 wt% and high amount of N are used for stabilization of the FCC austenite phase. For solid solution and precipitation strengthening, a high concentration combination of W, Co, Nb, Cu and other elements is added. Recently, it has been reported that the highly-alloyed steel Sanicro 25 exhibits excellent corrosion resistance combined with the highest creep strength at 700 °C among all heat-resistant austenitic steels commercially available today [1]. The promising potential of this alloy for high temperature applications led also to investigation of mechanical properties during more complex type of loading such as the low cycle fatigue, dwell-fatigue and thermo-mechanical fatigue. Polák and coworkers [7–12] have documented that after cyclic loading at high temperature, Sanicro 25 exhibits exceptional cyclic strengthening, leading to remarkably high saturated cyclic stress. In a very brief preliminary work [11], they have hypothesized that besides a substantial increase of dislocation density, nucleation of nanoscale precipitates and their interaction with mobile dislocations may also play a significant role in the cyclic strengthening behaviour.

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Table 1
The nominal composition of studied Sanicro 25 highly-alloyed austenitic stainless steel (in wt%). Composition of steel studied in this work is compared with the composition guaranteed by the producer [1].

	Fe	Ni	Cr	W	Cu	Co	Nb	Mn	N	Si	C
This work	42.9	25.0	22.5	3.6	3.0	1.5	0.5	0.5	0.23	0.2	0.1
Producer Min/Max	Rest	23.5 – 26.6	21.5 – 23.5	2.0 – 4.0	2.0 – 3.5	1.0 – 2.0	0.3 – 0.6	0.6 Max	0.15 – 0.30	0.4 Max	0.04 – 0.1

The purpose of this work is to show that two distinct nano-scale particle populations exist, one Cu-rich and the other Nb-rich, and to provide detailed insight into their atomic structure and relationships with the matrix. Probe aberration corrected HAADF-STEM imaging of the Moiré-like contrast and analysis of these experimental images supported by modeling and image simulations enabled, to our knowledge for the first time, thorough investigation of the dispersoid-like population of nano-scaled NbC particles that dynamically form during cyclic deformation. This is fundamental to an improved understanding of the overall microstructural changes and corresponding mechanisms leading to the exceptional high temperature cyclic strengthening of this alloy.

2. Experimental

The Sanicro 25 steel was supplied by Sandvik (Sandviken Sweden) in 150 mm diameter bars. The nominal composition (in wt%) of the material is given in Table 1. After machining of the crude shape of the specimens, they were annealed at 1200 °C for one hour and cooled in air. This state of material is referred to as “initial” in the text. All mechanical tests were performed using computer controlled electro-hydraulic MTS system equipped with hydraulic grips, split resistance furnace and high temperature axial extensometer with 12 mm base. Fully reversed strain-controlled cyclic loading with a constant strain rate of 2×10^{-3} s^{-1} at temperature of 700 °C was applied. Further information about the testing conditions can be found elsewhere [7–9].

The microstructure was investigated using scanning transmission electron microscopy (STEM). Thin plates were cut transverse to the gauge section of the bulk specimens by electrical-discharge machining and 3 mm diameter electrolytically polished discs were prepared with a double jet device TenuPol2. Details about the oriented TEM foils preparation can be found in [9]. For atomic resolution observations of inspected grains, the foils were tilted in order to perform high-angle annular dark-field (HAADF) zone axis imaging using a probe aberration-corrected FEI Titan^3 80–300 kV STEM. High spatial resolution energy dispersive X-ray spectroscopy (EDS) was conducted at 300 kV using an image-corrected FEI Titan^3 60–300 kV with a Super-X EDS detector, and utilizing the Bruker Esprit software. The detection system uses four silicon drift detectors that are located radially around the objective pole piece and specimen stage for improved collection performance. The presence of carbon and nitrogen was verified using electron energy-loss spectroscopy (EELS).

3. Results

3.1. Cyclic stress-strain response at 700 °C

Thorough study of the overall stress-strain response and the evolution of hysteresis loop shape under constant total strain amplitude loading both at room and elevated temperature was published earlier [7,8]. While the cyclic response at the room temperature is similar to the conventional austenitic steels, exceptional cyclic strengthening is reported at 700 °C. Cyclic plastic response of Sanicro 25 loaded in total strain amplitude control at 700 °C was compared with conventional 316 L austenitic steel loaded at 600 °C (more details about the material and testing can be found in [13]). Hardening/softening curves are plotted in Fig. 1a as stress amplitude σ_a versus number of cycles N. All tests were conducted until failure, where the number of cycles at failure of the specimen is designated as N_f. In case of conventional 316 L steel, after short initial hardening, saturated cyclic response prevails until failure. On the contrary, Sanicro 25 exhibits an extraordinary increase of cyclic stress that persists for a much longer fraction of the total fatigue life. This is demonstrated in Fig. 1b where the increase of cyclic stress in four different stages of fatigue life is plotted for all strain amplitudes. The increase of stress amplitude $\delta\sigma_a$ is defined as the difference between magnitudes of the stress amplitude in a particular cycle $N > 1$ and the first cycle $N = 1$. It is apparent that cyclic strengthening is present during the whole fatigue life in all tests of Sanicro 25 at 700 °C. The higher the applied strain amplitude, the more significant the increase of the cyclic stress is observed during the initial period of cycling. With further cyclic loading, the tendency to reach saturation of the cyclic stress is noticed, especially in the case of lower strain amplitude tested samples, i.e. samples tested for the highest number of cycles. Thermal exposure of specimens ranged from 153 to 6 h for the lowest and highest strain amplitude, respectively.

3.2. Microstructural changes as a result of cyclic loading at 700 °C

The initial microstructural state of the Sanicro 25 alloy and corresponding changes of dislocation arrangements as a result of cyclic loading were first reported in closely related studies [9,11]. A typical and representative low magnification scanning electron microscope (SEM) image of the overall microstructure in the initial state is shown in Fig. 2a. The average grain size, determined by the intercept method, was 60 µm; but, large grains of size up to 200 µm were found as well. After annealing at 1200 °C for 1 h, only one predominant primary precipitate is present in the microstructure, the complex nitride designated as Z-phase with a composition of (Cr,Nb)N as was documented previously [9]. The Z-phase exhibits very good stability at high temperatures since its dissolution starts between 1300 °C and 1450 °C. Particles of the Z-phase have been observed frequently in Nb stabilized austenitic steels containing a high level of nitrogen [9,14]. They are found both at grain boundaries and inside the grains with sizes varying from 100 to 400 nm. In addition, the presence of a very small amount of $M_{23}C_6$ chromium carbides has been reported in the initial state. However, according to Sourmail [14], the dissolution temperature of these carbides should be below 1100 °C, suggesting their presence after annealing is arguable.

In Fig. 2b, a bright field (BF) STEM diffraction contrast image (STEM-DCI) shows the microstructure of the initial state of the material. Annealing at 1200 °C for 1 h significantly decreases dislocation density. Only individual dislocations and pile-ups are observed, mostly tangled close to the incoherent Z-phase precipitates. Based on foil thickness measurement (t/λ) determined using EELS, the average dislocation density has been roughly estimated to be $\sim 9\times10^{12}$ m^{-2} in the initial state.

Cyclic loading leads to a significant change in the substructure of the alloy. First, the dislocation structure changes depending on the composition of the material, interstitial content, temperature, and the imposed plastic strain amplitude. It was reported previously, that at room temperature, surprisingly strong planarity of the dislocation slip prevails with significant plastic strain localization into thin deformation bands [9,15]. In the case of many other austenitic stainless steels, the stacking fault energy (SFE) was determined to be relatively low (lower