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On the origin of extraordinary cyclic strengthening of the austenitic stainless steel Sanicro 25 during fatigue at 700°C

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Abstract

The origin of the extraordinary strengthening of the highly-alloyed austenitic stainless steel Sanicro 25 during cyclic loading at 700°C was investigated by use of advanced scanning transmission electron microscopy (STEM). Along with substantial change of dislocation structure, nucleation of two distinct populations of nanoparticles was revealed. Fully coherent Cu-rich nanoparticles were observed homogeneously dispersed with high density along with nanometer-sized incoherent NbC carbides precipitating on dislocations during cyclic loading. Probe-corrected HAADF STEM imaging was used to characterize the atomic structure of nanoparticles. Compositional analysis was conducted using both EELS and high spatial resolution EDS. High temperature exposure induced precipitation of a high density of coherent Cu-rich nanoparticles while strain-induced nucleation of incoherent NbC nanoparticles leads to retardation of dislocation movement. The pinning effects and associated obstacles to dislocation motion prevent recovery and formation of the localized low-energy cellular structures. As a consequence, the alloy exhibits remarkable cyclic hardening at elevated temperature.

Keywords

steel; fatigue; scanning transmission electron microscopy (STEM)

1. Introduction

Austenitic stainless steels have a very wide spectrum of applications in different branches of the industry. They are used for design of equipment working both at room and low temperatures as well as high temperatures [1, 2]. In the field of coal-fired power generation, increased demand to improve the efficiency of power plants and thereby reduce carbon emissions leads to the need for new heat-resistant materials with improved high-temperature strength, enhanced creep properties, and high-temperature corrosion resistance at proposed increased high operating temperatures at 700°C [3].

One of the promising cost-effective candidate materials developed for use in future advanced ultra-supercritical (A-USC) coal-fired boilers is the austenitic stainless steel Sandvik Sanicro 25. This steel is based on the Fe-Ni-Cr alloy system with a high content of alloying elements: W, N, Co and Nb added (presumably for solid solution hardening), as well as high content of Nb, N, Cr and Cu (presumably for precipitation strengthening). The 22.5 wt.% Cr content results in good steam oxidation and hot corrosion resistance. High Ni content of approximately 25.0 wt.% and, relatively high amount of nitrogen contribute to the stabilization of the FCC structure.

Most of the austenitic steels commercially available today are capable of operational service temperatures up to 650°C. Highly-alloyed steel Sanicro 25 exhibits excellent high-temperature strength, creep properties and corrosion resistance at temperatures up to 700°C. To understand material characteristics and mechanisms leading to such performance, there is a serious need for the investigation of the inter-related effects of composition, microstructure, deformation mechanisms, and overall material response under static and cyclic loading conditions.

Recently, cyclic plastic response and low cycle fatigue behavior [4, 5] as well as surface profile evolution and fatigue crack initiation at room temperature [6, 7] of this material were reported. Creep properties [1, 8] and corresponding microstructural changes [9] after thousands of hours of steam exposure were also studied. However, detailed investigation of mechanisms governing high temperature cyclic behavior is still missing. Polák and coworkers [4, 5, 10, 11] have reported exceptional cyclic hardening, during low cycle fatigue at 700°C leading to remarkably high saturated cyclic stress. They have hypothesized that fine scale precipitates and their interaction with mobile dislocations may play a significant role in cyclic strengthening. The purpose of present work is to reveal further details of overall microstructural changes and corresponding mechanisms leading to the striking and exceptional high temperature cyclic hardening of Sanicro 25.

2. Experimental details

2.1 Material

The experimental material, Sanicro 25 austenitic stainless steel of grade UNS S31035, was supplied by Sandvik, Sweden in the form of the cylindrical rods of 150 mm in diameter. The nominal composition was (in wt.%) 0.1 C, 22.5 Cr, 25.0 Ni, 0.5 Mn, 3.6 W, 1.5 Co, 3.0 Cu, 0.5 Nb, 0.23 N, 0.2 Si and balance Fe. Cylindrical specimens for high temperature cyclic straining were machined with the axis parallel to the rod. The gage length was 15 mm and the diameter of the specimens was 6 mm. After the production of the crude shape of specimens, they were annealed at 1200°C for one hour and cooled in the air. This state of material is noted as “initial” further in the text.

2.2 Mechanical tests

Mechanical tests were performed using a computer controlled electrohydraulic 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

constant strain rate $2 \times 10^{-3} \text{ s}^{-1}$ was applied at 700°C . The saturated amplitude of plastic strain was evaluated. Further information about the testing conditions can be found elsewhere [4, 5, 10].

2.3 Transmission electron microscopy

The microstructure was investigated by means of transmission electron microscopy (TEM). Thin plates were cut perpendicular to the loading axis from the gauge length of the bulk specimens by electric-discharge machine. These were mechanically ground to produce thin foils of thickness of 0.08 mm, which were then punched out to produce disks having a diameter of 3 mm. The discs were then electrolytically polished using a double jet device TenuPol2. The electrolyte was composed of 95% of acetic acid and 5% of perchloric acid. The polishing conditions were 80 V-90 V, 0.2 mA and temperature of $13\text{--}16^\circ\text{C}$. Further details about the oriented TEM foil preparation can be found in [10].

The spatial arrangement of dislocations in grains was determined using the technique of oriented foils. Conventional transmission electron microscopy (CTEM) was performed using TEM Phillips CM12 working at 120 kV and using also JEOL 2100F scanning transmission electron microscope (STEM) operating at 200 kV. For atomic resolution observations inspected grains were tilted in order to perform high-angle annular dark-field (HAADF) zone axis imaging using a probe-corrected FEI Titan3 80-300 kV STEM. High spatial resolution EDS scans were conducted at 300 kV using an image-corrected FEI Titan3 60-300 kV with a Super-X energy dispersive spectroscopy (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 by electron energy loss spectroscopy (EELS).

3. Results

3.1 Initial microstructure

A representative view of the overall microstructure in the initial state is shown in Fig. 1a. The average grain size, determined by the intercept method, was $60 \mu\text{m}$; but, large grains of size up to $200 \mu\text{m}$ were also found. At the grain boundaries as well as inside the grains, large Nb-rich primary particles with size varying from 100 nm to 400 nm were observed. Reported previously [9, 10], these are nitrides designated as Z-phase with composition of (Cr, Nb)N. Particles of Z-phase have been observed frequently in Nb stabilized austenitic steels containing a high level of nitrogen [9, 12].

The crystal structure of the Z-phase for the stoichiometry CrNbN has been proposed as distorted body-centered tetragonal (space group $P4/nmm$) with lattice parameters $a = 3.04 \text{ \AA}$ and $c = 7.39 \text{ \AA}$ [12, 13]. In austenitic steels, the empirical formula is approximately $(\text{Cr}_{0.8}\text{Fe}_{0.2})(\text{Nb}_{0.9}\text{Mo}_{0.1})\text{N}$ [13]; however, the composition varies with the composition of the steel, and small concentrations of several substitutional elements (Mn, W) can be dissolved in Z-phase as illustrated for present case in Fig. 1b.

Z-phase is stable at high temperatures, and after annealing at 1200°C, it is the predominant precipitate since its dissolution temperature is between 1300°C and 1450°C, in accord with present results. Except for a small amount of nanometer-sized $M_{23}C_6$ chromium carbides, Z-phase was the only precipitate observed in initial state [9, 10].

3.2 Cyclic stress-strain response

Detailed investigation of the overall stress-strain response under constant total strain amplitude loading was reported earlier [4, 5]. In the present study, attention is placed on the cyclic stress-strain response at 700°C. Evolution of the hysteresis loop shape in Fig. 2a for total strain amplitudes 0.2% and 0.7% illustrates the significant increase of cyclic stress as a function of fatigue cycles. Cyclic hardening/softening curves of specimens cyclically loaded over a wide interval of total strain amplitudes are plotted in Fig. 2b as stress amplitude σ_a vs. number of cycles N . The initial increase of the stress amplitude with each cycle indicates a notable work-hardening effect. This is observed for all strain amplitudes. Higher the strain amplitude that is applied, the more significant and more rapid is the cyclic hardening. After the inflection point the hardening rate rapidly decreases and a tendency to reach saturation of cyclic stress is observed for all strain amplitudes. The possible substructural origins of this behavior are now presented.

3.3 Dislocation structure evolution

The stacking fault energy (SFE) in austenitic stainless steels is quite low (lower than 0.020 Jm⁻² [14, 15]) and as a consequence the dissociation distance between Shockley partial dislocations is large. Therefore, in the initial state of material, the dislocations tend to be present in planar arrays and pile-ups of individual dislocations and stacking faults, [10] as is shown in STEM low angle annular dark field (LAADF) diffraction contrast (STEM-DCI) image in Fig. 3a. Annealing at 1200°C for 1 hour leads to significantly decreased dislocation density. Most of dislocations observed are individual pile-ups or tangles close to the incoherent Z-phase precipitates or grain boundaries.

With cyclic loading, dislocation structure evolution strongly depends on imposed plastic strain amplitude, temperature and interstitial content. In closely-related studies [6, 7, 10], strong planarity of dislocation slip and plastic strain localization was reported for room temperature fatigue of Sanicro 25. At high temperatures, dislocation structures differ significantly. All grains are filled with a homogeneously distributed and high density of dislocations. Typical and representative arrangements are shown in Fig. 3. When compared to initial state, cycling with total strain amplitudes of both $\epsilon_a = 0.27\%$ and $\epsilon_a = 0.50\%$ leads to a notable increase of dislocation density. Evidence of cross-slip and climb of dislocations supports the hypothesis about thermally activated effects [16] contributing to the production of homogeneous, high dislocation density. Cyclic slip localization is suppressed. In contrast to conventional austenitic steels such as 316L [14, 17], no cellular structures were found indicating that localized dislocation rearrangement, usually responsible for cyclic softening at high temperatures, is not present in Sanicro 25.

3.4 Precipitation of strengthening nanoparticles

Cyclic straining at 700°C leads to substantial microstructural changes. The large number of alloying elements with high concentration in Sanicro 25 results in significant enhancement of diffusion effects and further precipitation of secondary phases. In steels with a high level of nitrogen that are stabilized by niobium, high mutual affinity of these two elements results in a fast Z-phase precipitation [9, 12, 13]. The presence of carbon is known to lead to rapid nucleation of numerous $M_{23}C_6$ chromium-rich carbides inside the grains; but, this occurs mostly at grain boundaries where they cause significant depletion of chromium content in the matrix, especially at low angle boundaries [10]. As reported earlier [12], carbides can be found already after very short aging times (less than hour at 750°C) even in stabilized steels.

An example of semicoherent, cuboidal $M_{23}C_6$ chromium-rich carbides nucleated within an austenite grain is shown in atomic resolution STEM-HAADF micrograph in Fig. 4a. The structure is viewed along the [011] zone axis. A FFT filtered image of interface (frequencies corresponding to the noise and the transmitted beam spot were excluded) demonstrates cube-on-cube orientation of carbide with the matrix in Fig. 4b. In detail, the experimentally obtained atomic structure is compared to a $Cr_{23}C_6$ model [24] created in the Crystal Maker software. In the model, carbon atoms are colored in black and chromium atoms in pink (Fig. 4b). Fast Fourier transformation patterns (Fig. 4c) determined from matrix and $M_{23}C_6$ area confirms a cube-on-cube orientation. In reciprocal space, the shorter distance to the carbide diffraction spots (by a factor of 3) relative to that of the FCC matrix corresponds well to the reported lattice parameter of $M_{23}C_6$, which is three times larger than the lattice parameter of austenitic FCC matrix [12]. Representative EDS analysis of an array of $M_{23}C_6$ carbides precipitated at low angle grain boundary is shown in Fig. 4d, indicating that these carbides can also nucleate heterogeneously on such boundaries.

In addition to the phases reported in present study, Zurek et al. [9] observed also Cr_2N chromium nitrides, μ -phase of the type Fe_7W_6 and small amount of Laves (W-rich) phase. However, these phases were detected after ageing of Sanicro 25 for several thousands of hours. Fatigued samples in this work were aged only up to 153 hours (the lowest strain amplitude $\epsilon_a = 0.2\%$) and none of the latter phases were detected. Time needed for their nucleation and coarsening is probably longer than reached during cyclic loading.

Study of deformation microstructure [10] revealed possible interactions of dislocations with nanometer-sized microstructural objects. Therefore, high spatial resolution EDS mapping was performed on a specimen cyclically loaded with the total strain amplitude $\epsilon_a = 2.7 \times 10^{-3}$ (4482 cycles to fracture, i.e. 23 hours at 700°C). As shown clearly in Fig. 5, two different populations of nanometer-sized particles embedded in the matrix are revealed – particles rich in copper and particles rich in niobium. They are discussed in following chapters.

3.4.1 Cu-rich nanoparticles—After cyclic loading, the spherically-shaped copper-rich particles are numerous and homogeneously distributed in the matrix. They were previously observed in several austenitic stainless steels [8, 9]. In the present study, a combination of both atomic resolution Super-X EDS mapping and STEM HAADF imaging (using low camera length, with inner-angle cut off 55 mrad and outer angle cut-off 370 mrad, in order to enhance Z-contrast) was used for characterization of Cu-rich particles.

First, the initial state of material was inspected by EDS analysis. Raw data were extracted from the original spectral maps and quantified using the Bruker Esprit software and the Cliff-Lorimer k-factor fit. No Cu-rich phase has been detected. Quantified maps showed only a homogeneous, Cu-enriched solid solution with about 3.4 at.% in composition in average. This result is fully in agreement with work reported by Chi et al. [18], who used 3D atom probe tomography (APT) for compositional analysis of Cu-phase precipitation. After solid solution treatment, all Cu atoms dissolved in the austenitic matrix and formed a supersaturated solid solution. It is also noted that a similar distribution and density of particles was also found in samples extracted from the grip section of the same fatigue specimen, indicating that the Cu-rich particles are resulting from a thermally-induced decomposition of the austenite matrix.

In Fig. 5b, an EDS line scan across two Cu-rich particles located close together is shown. The composition (in atomic %) is plotted as a function of distance. It is evident, that after 23 hours of exposure at 700°C and superimposed cycling, spherical regions are formed. They are enriched in copper while depleted in the other elements such as Fe, Cr and Ni. Further EDS analysis in the matrix revealed 1.8 at.% of Cu, i.e. notable depletion when compared with the initial state. This again corresponds closely to the APT results of Chi et al. [18]. Increase of temperature to 700°C and an apparently high chemical driving force in the supersaturated solid solution induces rapid diffusion of copper atoms into Cu-rich regions. As the aging time continues, the base matrix elements (Fe, Cr, Ni) diffuse away and the Cu-rich nanoprecipitates are formed.

Probe-corrected STEM HAADF imaging was used to obtain crystal structure characteristics. As shown in Fig. 6a, two types of round objects are observed – with darker and with brighter contrast relative to the matrix. Further analysis has shown that the dark contrast are cone-shaped holes which were previously occupied by Cu-phase particles located close to the surface, but were electrochemically attacked and removed during the sample preparation. The bright contrast objects of similar size scale are the Cu-rich nanoparticles remaining embedded in the matrix. In HAADF Z-contrast imaging, the intensity of atomic columns directly reflects their mean square atomic number (Z). Since Cu has higher atomic number (29) than Cr (24), Fe (26) and Ni (28), Cu-rich regions have slightly brighter contrast than the matrix. By counting only cone-shaped holes and dividing that number by two (accounting for holes at the top and at the bottom of the TEM foil), the surface areal density of particles was determined to $3.2 \times 10^{14} \text{ 1}/\mu\text{m}^2$. Incorporated EDS mapping and measurement of foil thickness by EELS also enabled determination of particle volume density, which was about $(1.1 \pm 0.4) \times 10^{22} \text{ 1}/\mu\text{m}^3$. The average size of particles after 23 hours of ageing at 700°C was 7.4 nm, median was 7.0 nm, minimum and maximum were 4.6 nm and 15 nm, respectively.

It was reported earlier [20, 18.] that in conventional steels Cu-rich nanoparticles are semi-coherent with the matrix, since misfit dislocations or ledges were found at the interface. However, in present work, no discontinuities in atomic column spacing across the precipitate/matrix interface were observed. Pure copper has same cubic $Fm\bar{3}m$ (space group 225) crystallographic structure as the austenitic matrix with a lattice parameter $a_{\text{Cu}} = 3.615 \text{ \AA}$ (JCPDS 04-0836). We have used neutron powder diffraction on the instrument

MEREDIT@NPI for precise measurement of the Sanicro 25 austenitic matrix lattice parameter in the initial state prior to high temperature exposure. It was evaluated to be $a_\gamma = 3.60692(8) \text{ \AA}$, which is slightly larger when compared to conventional steels [18]. Interestingly, in highly-alloyed Sanicro 25 steel, pure copper would have a small positive lattice misfit of only $\delta = 0.22\%$, which is apparently sufficiently small to enable perfect coherency between particles and matrix that has been observed in the present study.

3.4.2 Nb-rich nanoparticles—Nb-rich nanoparticles were found after cyclic loading with $\epsilon_a = 0.27\%$ at 700°C (23 hours of ageing, see Fig. 5a). They are smaller than the Cu-rich precipitates with an average size of about 5.1 nm. Median was 5.1 nm and minimal and maximal diameter was 3.8 nm and 6.7 nm, respectively. Contrary to the Cu-rich nanoparticles, their distribution is notably inhomogeneous. They are predominantly found in aggregations of a few particles gathered together and are very rarely observed as isolated separate objects. Furthermore, in many cases they are arranged along dislocation lines, as will be discussed further.

Areas with strong Nb content detected by EDS (as shown for example in the line scan in Fig. 5c) were analyzed using atomic resolution HR-TEM and STEM. In HR-TEM, for both $[001]$ and $[011]$ zone axes distinctive Moiré fringes were found at assumed nanoparticle locations.

Moiré fringes are parallel lines formed by the interference of diffracting crystal lattice planes from two overlapping crystals, which generally might have different spacing and orientation [21, 22]. Shown in Fig. 7 is a $[001]$ zone axis HR-TEM phase contrast image showing the Moiré fringes and corresponding FFT obtained from the particle region. Along with the intense FFT spots from the austenite matrix, weaker satellite reflections are also observed belonging to a second lattice, accompanied by double diffraction reflections. The patterns indicate that the precipitates have an FCC crystal structure oriented in a cube-on-cube relationship with the austenite matrix.

As described by kinematical theory, in case of semi-coherent or incoherent misfitting precipitates, a waveform in the lattice spacing could potentially generate both positive- and negative-displacement satellite reflections in the diffraction pattern with an offset based upon the planar periodicity [23, 22, 24]. The FFTs (see Fig. 7) of both HR-TEM and STEM HAADF images of the precipitate demonstrate that these satellites result from the presence of nanoparticles, as a similar strict periodicity exists in the particle/matrix interface due to the positive lattice misfit.

Based on the conclusion that these are in fact Moiré fringes, the lattice plane misfit can be measured by use of the following equation [23, 25, 26] for the period of modulation, λ_m :

$$\lambda_m = \frac{ha}{h^2 + k^2 + l^2} \frac{G}{\Delta G}, \quad (1)$$

where a is the lattice parameter, G is the distance of the $(h k l)$ spot from the $(0 0 0)$ spot, and G is the distance of a satellite spot from the main $(h k l)$ spot. Solving for λ_m for measured reciprocal values from a $\{002\}$ -type of reflections reveals a waveform periodicity of ~ 1.22 . Thus, the lattice parameter of precipitate is 1.22 times larger than the lattice parameter of the

matrix, indicating positive misfit of about 22%. Using both the lattice parameter of austenitic matrix and, this matrix/precipitate lattice misfit, the precipitate lattice constant is estimated to be about 4.41 Å.

Thus, the prominent features of these precipitates – (a) Nb-rich, (b) observation of Moiré fringes, and (c) corresponding FFT diffraction patterns indicating FCC structure with cube-on-cube orientation and positive lattice misfit - are consistent with the results published earlier by Sourmail [12] and Haddrill et al. [27]. In the Fe-Ni-Cr based steels with high carbon and nitrogen content, they report a strong tendency for nucleation of NbX (X = C, N) precipitates since Nb has high affinity for both C and N. Possible phases have a NaCl FCC structure with lattice parameters of NbN and NbC $a = 4.4$ Å and $a = 4.47$ Å, respectively [12]. To identify, which type of nanoparticles is present in Sanicro 25, EELS analysis was used for the detection of light elements. While carbon was verified in the regions of the Nb-rich nanoprecipitates, *no* nitrogen was found. Nucleation of NbN phase is presumably less probable since the coarse Z-phase (CrNbN) primary precipitates probably consume most of the available N. Therefore, the experimental evidence suggests the presence of NbC nanoparticles.

Several authors [21, 23, 28] describe NbC nanoparticles as coherent or semi-coherent. Nevertheless, if both lattice misfit and particle size are taken in account, coherency with matrix is arguable. No misfit dislocations at the particle-matrix interface, which might be able to accommodate significant lattice misfit, were observed in this work.

In a closely-related study [30], STEM HAADF image simulation based on the model of an *incoherent* NbC nanoparticle with austenite matrix was performed to validate structure of nanoprecipitates and the observed Moiré-like contrast. Modeling and simulation has shown excellent agreement with experimental results.

The evolution of strain-induced NbC precipitates in a model austenitic steel compressed at high temperatures was investigated by Poddar et al. [21]. Depending on the length of hold times interrupting high temperature uniaxial straining, different stages of particle nucleation were observed. Longer hold times led to well-defined, faceted precipitates about 10 nanometers in size, while after short interruptions of less than 3 seconds substoichiometric, cluster-like nanoparticles about 5 nm of diameter were observed.

To explore, how the precipitation of NbC nanoparticles is affected by high temperature cyclic loading compared with static (thermal exposure) the grip part of specimen was studied and results were compared to observations from the gage section. A comparison of typical substructure features is shown in Fig. 8. In both cases, dislocations and stacking faults are covered by nucleated NbC precipitates. In Fig. 8a and in detail in 8b, nanoparticles approx. 6 nm in size are densely configured along a dislocation. At high magnification, a distinctive Moiré-like pattern is observed. The same arrangements of NbC precipitates were found also in grip part of specimen. However, in the latter case, they are much larger with diameter up to about 20 nm and they are detected exclusively on lattice defects as illustrated in Fig. 8c. A pile-up of $\frac{1}{2}\langle 101 \rangle$ edge dislocations is covered by a high density of NbC particles. Relative to the grip section results, another important difference is that,

aggregations of small NbC nanoparticles are found in the cyclically strained gage section, which are not decorating dislocations. However, considering their clustered arrangement, it is hypothesized that these small groups of nanoparticles remain after dislocations detached from them under cyclic loading conditions. Their dispersion is inhomogeneous when compared to Cu-rich precipitates. However, they can act as obstacles for subsequent dislocation movement. A typical example of pinning interaction with moving dislocation is shown in Fig. 8d. STEM HAADF image with enhanced strain contrast (long camera length of 230 mm used) of dislocation lines illustrates pinning of $\frac{1}{2}[01\bar{1}]$ mobile edge dislocation by two NbC precipitates of size about 6 nm.

Because of large positive misfit, it is further surmised that precipitation of NbC particles in the defect-free austenite matrix is extremely difficult. However, nucleation clearly does occur at lattice defects, where part of the strain energy can be released by replacement of dislocation line length and strain field with the precipitate nucleus. This also helps to overcome the nucleation barrier and enables the existence of nanoprecipitates as incoherent particles in austenite matrix.

4. Discussion

The initial condition of the Sanicro 25 alloy, i.e. the chemical composition and microstructural state, plays a fundamental role in the evolution of deformation microstructure and corresponding mechanical response during cyclic loading at high temperature. The present work has shown that a high number and content of alloying elements in Sanicro 25 leads to unusual cyclic behavior, not observed in the case of conventional stainless steels [14, 17]. Fatigue at 700°C facilitates diffusion and precipitation effects resulting in the nucleation of two distinctive populations of nanoparticles embedded in the matrix – particles rich in copper and nano-sized NbC carbides.

To discuss how significant is the influence of these nanoparticles on the extraordinary cyclic hardening at high temperatures it is necessary to outline all possible strengthening mechanisms that may be acting. In each cycle, the overall yield stress is determined by several components. First, grain boundary strengthening should be considered. The average grain size of the Sanicro 25 is 60 μm . Since this grain size is relatively large, then, according to the Hall-Petch equation, grain effects can be considered as negligibly small. As was discussed previously, Sanicro 25 presents a higher content of W, Co, N and Nb. Therefore, solid solution strengthening might be more pronounced. Some conventional austenitic steels exhibit solute segregation to dislocations causing pinning of their movement. These effects are mostly observed around temperatures close to 400°C. However, Sanicro 25 was tested at 700°C and no evidence of solute atmosphere formation via EDS analysis or and locking effects as exhibited by dynamic strain ageing (DSA) has been found so far. The third component to be considered is the stress corresponding to lattice friction. This contribution usually plays an important role at room temperatures, but should be negligible at high temperatures.

In the present case, the mutual interaction of two remaining strengthening mechanisms, forest dislocation hardening and precipitation strengthening, appear to play a fundamental

role in the high temperature cyclic loading. The dislocation density is substantially increased in cycling with all strain amplitudes [10]. Both cross-slip and climb of dislocations are thermally enhanced, with dislocations gradually filling the whole volume of the grain. As the dislocation density rises with each cycle, movement and mutual dislocation-dislocation interactions become more complex and important. Based on the Taylor relation, dislocation forest hardening then can contribute significantly to an increase of the cyclic stress.

The mode of NbC carbide precipitation is profoundly affected by plastic deformation. The application of cyclic strain during testing introduces the necessary density and configuration of matrix dislocations. The increased, homogeneous distribution of dislocations within the grains then causes a significant acceleration in the nucleation, growth and coarsening of precipitates, possibly aided by accelerated pipe diffusion of solute elements through dislocation cores [21]. Despite the continuous cyclic tension-compression loading, cluster-like, incoherent NbC nanoparticles rapidly nucleate on some dislocations, since the time needed for their precipitation is short. Dislocations are then prevented from further movement as a result of extensive pinning by the dispersion of NbC particles nucleated on them (see Figs. 8a and 8b).

As was shown in Fig. 8d, not all of the existing particles are decorating dislocations, indicating that it is possible for dislocations to break away from the NbC precipitates. Unpinned dislocations will leave behind a non-uniform distribution of nanoparticles demarking the former positions of the dislocation lines. Once mobilized, the dislocations will nonetheless experience a dense array of pre-existing precipitates that retards their motion, and makes likely the subsequent arrest and additional heterogeneous nucleation of additional NbC particles along the dislocation lines. Provided a sufficient source of free Nb and C in solid solution, it is possible that this process could repeat numerous times, on an individual dislocation basis, and lead to continually increasing density of NbC obstacles in the microstructure as a function cyclic loading.

Based on the present post-mortem STEM-DCI observations, these particles are smaller than precipitates found gathered along completely pinned dislocation lines (e.g. in the sample after only thermal annealing). This further suggests that once detached from dislocations, those particles do not coarsen significantly. However, they can act further as obstacles for dislocation movement (see Fig. 8d). Being incoherent and in aggregated configurations, they are difficult to be overcome by dislocations even when climb bypass is active. Indeed, these particles appear to present attractive interactions with dislocations (e.g. Fig. 8d), analogous to the potent high temperature strengthening that can be achieved by incoherent particles in oxide dispersion strengthened (ODS) alloys.

A third synergistic effect contributing to the dynamic strengthening is precipitation of fully coherent Cu-rich nanoparticles uniformly distributed in the matrix with an extremely high number density. As they are coherent with the matrix, gliding dislocations can readily cut them. It is interesting to note that pure copper is softer than austenitic matrix, with a shear modulus approximately half that of conventional austenitic steels [31]. As a consequence, it might be expected that they can provide attractive sites (in terms of elastic strain energy) for

shearing dislocations. . A more quantitative description of this interaction is presently in progress.

The permanent increase in stress levels with the number of cycles in fatigue of Sanicro 25 differs from the cyclic response observed for standard austenitic stainless steels. In these solid-solution-hardened alloys, a so called “plateau” cyclic stress level behavior occurs and is connected with the development of dislocation cell structure as observed in conventional 304 and 316 steels at 650°C [23, 32, 33]. As a consequence of thermally enhanced cross-slip and climb, increased dislocation-dislocation interactions lead to localized reordering and formation of tangles and later dislocation walls. With further cycling, walls evolve into a well-developed low energy configurations called dislocation cells [23, 34, 35]. In Sanicro 25, a radically different dislocation structure develops, with a remarkably homogeneous distribution of dislocation of high density. This general substructure characteristic suggests that dislocations are fundamentally controlled more by their mobility than by interdislocation forces (leading eventually to dislocation cell development). The intensive precipitation of the coherent, high density Cu-rich phase along with incoherent NbC nanoparticles identified in this work is expected to lead to significant retardation of dislocation movement. The pinning effects and associated obstacles to dislocation motion prevent normal recovery processes, and the conventional development of low-energy cellular structures. As a consequence, this alloy exhibits extensive cyclic hardening, even at elevated temperatures.

5. Conclusions

Study of the origin of the extraordinary hardening of the highly-alloyed austenitic stainless steel Sanicro 25 during cyclic loading at 700°C by use of advanced scanning transmission electron microscopy leads to the following conclusions:

- Cu-rich nanoparticles precipitate homogeneously with high volume density in the matrix as a result of elevated temperature. They have FCC structure and are coherent with the austenitic matrix with positive lattice misfit only 0.22%.
- Elevated temperature along with the high dislocation density facilitates rapid precipitation of NbC nanoparticles on dislocations and stacking faults. Larger particles are found along dislocation lines, smaller precipitates in aggregated groups from which dislocation was detached as a result of cyclic stress. They can act as obstacles for dislocation movement.
- The nanoparticles act as obstacles to dislocation motion and prevent reordering of dislocations. Low-energy cellular structures are not formed and homogeneous high dislocation density structure is characterized by a high amount of dislocation-dislocation interactions. As a consequence, material exhibits extraordinary cyclic hardening leading to the remarkably high saturated cyclic stress at 700°C.

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Figure 1:

Initial state of material. (a) SEM micrograph (backscattered electrons mode) of electrolytically polished surface of the Sanicro 25 after annealing for 1 h at 1200°C and cooling in air. Z-phase precipitates are located at the grain boundaries and also inside the grains. (b) STEM HAADF image of Z-phase particle (bright contrast) embedded in the austenite matrix. EDS is showing enrichment on Cr, Nb, N and also Mn and W in the precipitate. On the contrary, Fe, Ni, Co and Cu are depleted.

Figure 2:

(a) Cyclic hardening curves in constant total strain amplitude loading at temperature of 700°C. Stress amplitude vs. number of cycles is plotted. (b) Evolution of the hysteresis loop shape with cycling at total strain amplitudes 0.2% and 0.7%.

Figure 3:

(a) STEM LAADF micrograph of representative dislocation structure observed in initial state. As a result of annealing, dislocation density is very low; (b) CTEM BF image showing increased homogeneous high dislocation density distribution in samples cycled at 700°C with $\epsilon_a = 0.27\%$; (c) ditto with $\epsilon_a = 0.50\%$.

Figure 4:

Specimen cycled with $\epsilon_a = 0.27\%$ (aged 23 hours at 700°C). (a) STEM HAADF micrograph taken close to [011] zone axis showing $M_{23}C_6$ chromium carbide nucleated in austenitic matrix. In the bottom right, incoherent NbC nanoparticle precipitated. (b) Filtered image showing $M_{23}C_6$ matrix interface. In detail, experimentally obtained atomic structure of carbide is compared with the Crystal Maker software model. Black are carbon atoms, pink are chromium atoms. (c) Comparison of FFT taken from the matrix and $M_{23}C_6$ area. (d) STEM EDS mapping of $M_{23}C_6$ precipitates aggregated at the low angle grain boundary, which are rich in Cr, C and Mn.

Figure 5:

(a) High spatial resolution STEM EDS map showing distribution of Cu-rich and Nb-rich nanoparticles. (b) Line scan across two Cu-rich nanoparticles illustrating Cu atoms enrichment and depletion of main austenite matrix elements, Fe, Ni, Cr. (c) Line scan across Nb-rich nanoprecipitate showing strong Nb EDS peak.

Figure 6:

[011] zone axis STEM HAADF Z-contrast image showing (a) comparison of Cu-rich precipitates (bright contrast) and cone-shaped holes in the matrix where precipitates were electropolished out (dark contrast). (b) Atomic resolution image of coherent Cu-rich nanoparticle embedded in the matrix. Region enriched in copper atoms is brighter than surrounding austenite matrix.

Figure 7:
HR-TEM image of NbC particle viewed along [001] zone axis. Comparison of FFT diffraction patterns from NbC precipitate and matrix. The image is complemented by schematic drawing showing the difference between spacing of spots corresponding to both crystal lattices.

Figure 8:

STEM HAADF image showing (a) NbC particles nucleated on the dislocation viewed along [001] zone axis; (b) detail of Moiré-like pattern observed in locations where NbC particles are present; (c) bright field image of NbC nanoprecipitates nucleated at edge dislocations in grip part of specimen; (d) [011] zone axis STEM HAADF image with enhanced strain contrast (a large camera length 230 mm was used) showing two NbC particles (marked by black arrows) pinning $\frac{1}{2}[01\bar{1}]$ edge dislocation. A distinctive bowing of the dislocation line between the particles is noted.