PAUL SCHERRER INSTITUT

Report on the thesis manuscript entitled

High temperature deformation mechanisms

submitted by Milan Heczko

This PhD work deals with the low cycle fatigue behavior of two high-alloy austenitic steels: Sanicro 25 and Manaurite XTM. These two alloys are used for high temperature applications, in the range 700 °C to 800 °C, which are temperatures significantly higher than the maximum operation temperature of the conventional austenitic steel 316 for example. Sanicro 25 is foreseen for applications in thermal power plants and Manaurite XTN has been developed for ethylene cracking furnace. Previous studies showed that creep performance and strength of Sanicro 25, resulting from precipitation of complex nitrides, is superior to several conventional austenitic steel and other nickel-based alloys. For the time being, investigations on Sanicro 25 have been essentially focused on creep performance and microstructural stability. As far as Manaurite XTM is concerned, the fatigue behavior is poorly documented. The main objective of this PhD thesis was to gain insight into the cyclic behavior of these high-alloy austenitic steels at room and elevated temperature in relation to their initial and deformed (at the end of fatigue life) microstructures. The PhD manuscript is articulated around four main sections called respectively: “Current state of knowledge”, “Experiment”, “Results” and “Discussion”.

Findings:

The section “Current state of knowledge” introduces the studied materials, their respective industrial applications, and the technical issues, which they face. A lot of basic information is provided on lattice defects, including point defects, dislocations, interfaces, strengthening mechanisms, dislocation-obstacles interactions, and nature of interfaces. The standard models of crack initiation and propagation in cyclic deformation based on dislocation mechanics are reviewed along with the typical formation of dislocation arrangements, like the persistent slip bands.

The “Experiment” section describes briefly but adequately the geometry of the specimens tested, how they were extracted from the tubes, the testing machine and all the necessary information regarding the testing conditions. The preparation of the SEM and TEM specimens is also presented as well as the used microscopes.

The results are presented in the section “Results” in a very systematic way, starting with a description of the non-deformed microstructures of the two alloys. Sanicro 25 presents an equiaxed grains structure with complex nitrides (Z-phase). Small precipitates are located at the interior of the grain and the largest ones are found along the grain boundaries. Chain like arrangements of these precipitates were also observed. Manaurite XTM has a high chromium and nickel contents and it presents a dendritic structure with a high density or precipitates along the grain boundaries and aligned within the columnar grains.

The mechanical behavior in terms of tensile and cyclic deformation at room temperature and 700 °C is then presented through representation of the cyclic hardening/softening curves, plastic strain amplitude versus cycle number, cyclic stress-strain curves, Coffin-Manson plot, and Wöhler plots. For the Manaurite the anisotropy effects on the fatigue behavior were also studied and are reported here. There are anisotropic effects revealed by tensile tests as well as by the effects on the fatigue properties. (It seems to me however that the data points for the tangential and radial directions reported in Figure 9.10 are not consistent with the cyclic curves in Figure 9.8.) For both alloys, the fatigue life at 700 °C is shorter than at room temperature. Interestingly, a very large cyclic hardening was found for Sanicro 25 °C at 700 °C leading to a higher cyclic stress-strain curve than that at 20 °C. Such a behavior was not observed for Manaurite.

Details microscopical observations of the dislocation microstructure and precipitates evolution during cyclic loading for selected low and high strain amplitudes were conducted. At low strain amplitude ($3.5x10^{-3}$) and room temperature for Sanicro 25, planar dislocation microstructures with essentially one slip system active were observed with alternated regions of dislocation rich bands and areas free of dislocations. At room temperature and high strain amplitude ($7x10^{-3}$), planar dislocation arrangements were still observed but, in this case, double and triple slip was identified. In the same time, dislocation rich bands developed as for the low strain amplitude condition. In addition, at some locations, ladder-like microstructures were found. At high temperature for low and high strain, a very high density of dislocations is reported. In particular, the areas between the bands also contain a high density of dislocations. Estimates of the dislocation density were done. A details characterization of the precipitates was performed and a numbers of different features were identified: Cr-rich carbides, Cu-rich precipitates whose volume density and diameter were measured for three tests with different strain amplitudes (different experiment durations) that will serve as basis for a discussion on nucleation and coarsening behavior. The distribution of Nb-rich precipitates was also investigated on the same three specimens used of the characterization of the Cu-rich precipitates. The nature of the interfaces between those precipitates on the matrix was also characterized in details to determine the contribution to the strengthening mechanisms. It is worth to emphasize here that sophisticated electron microscopy techniques were employed for this purpose.

As far as the microstructures of Manaurite after fatigue experiments is concerned, observation at low ($3.5x10^{-3}$) and high strain amplitudes ($7x10^{-3}$) were also carried out. A careful selection of the TEM lamella along the central axis of the dendrite was done to avoid the long-range stress field associated with the serrated grain boundaries of this material. No clear evidence of strain localization was found at 20 °C. At high temperature, only the low strain amplitude deformation was investigated where no strain localization was observed either. Many $M_{23}C_6$ carbides precipitated during cyclic deformation both in the matrix and along dislocations while no nanoscopic features were observed as a result of precipitation in the matrix.

In the “Discussion”, a comparison of the mechanical properties between the two investigated alloys is done in the light of the obtained results. The comparison is further extended to other materials. The mechanisms of crack initiation at room temperature for Sanicro 25 is associated with plastic deformation localization in PSB leading to corresponding PSM with formation of intrusions/extrusions. The shorter fatigue life of Manaurite XTM at room temperature is, in contrast to Sanicro 25, related to the observed cracking taking place at brittle eutectic primary carbides, with cracks propagating into the matrix. Different mechanisms occurs at high temperature, where slip localization does not appear as the origin of cracking but rather oxidation of the grain boundaries results in intergranular cracking for Sanicro 15. The longer life if Manaurite XTM at high temperature is attributed to the high Cr content providing at better oxidation resistance. These interpretations of the cracking mechanisms are well discussed and supported by the microstructural observations. The strong cyclic hardening of Sanicro 25 at high temperature is compared with literature data of fatigue tests conducted either with dwell time or in thermos-mechanical mode where an exceptional cyclic hardening was also evidenced. The origin of this cyclic hardening is discussed and interpreted as the result of: 1) the precipitation of Cu-rich precipitates (Cu being in supersaturation after the rapid cooling in air following the annealing at 1200 °C) and, 2) the formation of Nb(C,N) features during active deformation, with nucleation occurring along dislocation lines that promote nucleation by reducing the strain energy of the incoherent interface between the particle and the matrix. The cyclic hardening is then decomposed into different contributions, namely solid solution, coherent Cu-rich precipitates, incoherent Nb(C,N) precipitates, forest hardening. Estimates of these different contributions, added linearly, revealed that the forest dislocation hardening represents the main contribution to the total cyclic hardening. The subsequent reduction of dislocation mobility prevents the formation of low energy configuration and corresponding annihilation mechanisms. The different high-temperature fatigue behavior Manaurite XTM is due to the fact that the Cu-rich and Nb(C,N) are not observed to form, since the high Cr content in this alloys may promote the formation of $M_{23}C_6$ at the expense of other phases.

Assessment :

The PhD manuscript presented by Mr. Heczko is well organized and reads pleasantly. It represents a major contribution in the understanding of the fatigue behavior at high temperatures of Sanicro 25 and Manaurite XTM for which a limited number of data exists. A significant amount of good quality mechanical tests and microstructural observations were performed, which are well within the expected amount of data for a PhD thesis. The numerous experimental techniques used for this work clearly shows that Mr. Heczko is a competent experimentalist, in particular he possesses excellent skills in TEM. A substantial effort was done to link the fatigue behavior in general, fatigue life, hardening/softening behavior, temperature dependence, with the end of life microstructures. This in turn indicates a solid background in physical metallurgy of Mr. Heczko.

On a little less positive note, from my point of view, the section “Current state of knowledge” is too much oriented towards a basic description of defects and resembles more a textbook than being a real literature survey on the investigated materials. I would also have appreciated to have a “Conclusions” section that highlight some perspectives and not being a list summarizing the main findings. In any case, the good quality of the many results presented and the solid interpretation and discussion of the data largely outweighs the above-mentioned weaknesses and **I recommend without doubt acceptance of the PhD thesis**.

Shortened version of the Thesis

The shortened version presents a summary of the thesis. It explains the aims of the work, describes the main results obtained, provides a short discussion of the results and gives the conclusions. A reader going through the shortened version will get a good picture of the extent of experimental work realized and of the key findings of the thesis. **Thus the shortened version can also be accepted in the present form.**

Questions:

For the PhD defense presentation, I would appreciate Mr. Heczko addressing the following questions/points.

In Figure 8.3, one can see that for many cycle hardening/softening curves of Sanicro 25 the stress amplitude increases at the end of the tests at 700 °C, and only at 700 °C. I suspect that the main crack leading to failure was not between the measured gage length (within the distance between the contact points of the ceramic rods). Have you the checked the location of the specimen failure, i.e., within gage length, within measured gage length or within the specimen shoulder? Can you give some clues why this phenomenon happened? and if it may have some consequence on the fatigue life?

1) The cyclic stress-strain curves were constructed with the stress and plastic strain values at half-life, referred as saturated vales. Except for few cases at room temperature for Manaurite XTM, the stress amplitude never reaches a saturated value: it keeps either decreasing or increasing. It would be interesting to see the plots of the derivative functions defined as $d\sigma_a/d(\varepsilon_{a,c})$ and $d\sigma_a/d\varepsilon_{p,c})$, where $\varepsilon_{a,c}$ is the cumulated total strain ($=2N\varepsilon_a$) and $\varepsilon_{p,c}$ is the cumulate plastic strain defined at a given cycle N is

$$\varepsilon_{p,c} = 2\sum_{i=1}^{N} \varepsilon_{p,i}$$

I am wondering whether all the curves with different strain amplitudes would degenerate into a single “master-curve”.

2) The formation of NbC nano-features was shown to require high temperature and plastic deformation. These features precipitate because the Nb and C contents in solid solution is high after the final heat-treatment. One can imagine to produce this material through a completely new thermo-mechanical treatment involving a high temperature deformation processing to form a high concentration of dislocation nucleation sites for the fine NbC features and to have all Nb and C homogeneously precipitated in the final product. Is such an approach a feasible solution for Sanicro 25? This question is made in the more general context of the perspective for future research based on the knowledge acquired in this PhD work.

Villigen, the 20th of November 2018 Dr. P. Spätig

P. Spätig