MODELING OF THE MICROSTRUCTURAL EVOLUTION IN CR-MO STEELS DURING TEMPERING AND HYDROGEN EXPOSURE

Sabine M. Schlögl
Fraunhofer Institute for Mechanics of Materials, D-79108 Freiburg, Germany

Summary
Hydrogen attack is a dangerous material degradation process that occurs in steels subjected to high pressures of hydrogen at elevated temperatures. A detailed study of the coupled processes responsible for hydrogen attack requires a combination of continuum mechanics with solid solution thermodynamics, kinetics and chemistry. This paper is concerned with the development of numerical models that combine these ingredients.

INTRODUCTION

Cr-Mo steels consisting of a ferritic matrix and alloy carbides can suffer from hydrogen attack when they are in contact with a hydrogen containing atmosphere. It is the combination of high hydrogen pressure and high temperatures which leads to the nucleation of cavitities at the grain boundaries and the formation of methane. The methane-filled cavities grow, which finally can result in intergranular failure. The objective is to develop models which incorporate several processes involved in hydrogen attack such as substitutional and interstitial diffusion in the ferrite, the chemical reaction at the cavity–ferrite interface, the movement of the carbide-ferrite interfaces due to the dissolution of carbides as well as the creep and diffusional deformation. First, a relatively simple one-dimensional model is presented which takes into account these processes within the framework of a multi-component, multi-phase continuum description. Secondly, the first steps in the development of a finite element code for a more sophisticated microstructural model is addressed where the spatial arrangement of the carbides is taken into account. These two models are applied to predict the evolution of the carbides in a Cr-Mo steel during tempering and their outcome are compared to find out whether the simple model is sufficient.

ONE-DIMENSIONAL MODEL

The one-dimensional (1D) model presented in [1] consists of three parts. Submodel 1 describes the dissolution of carbides as well as the diffusion of the substitutional elements and of C in the ferrite away from the carbide. Submodel 2 takes care of the chemical reaction that takes place inside the cavity once diffused carbon atoms meet hydrogen. Finally, submodel 3 handles the growth of the cavity due to the methane pressure built up during the chemical reaction.

The microstructure is represented by means of a spherical unit cell of radius r_o. A total of N carbides with radius ρ^j are embedded in the ferritic matrix (α-Fe) of the unit cell. The spatial arrangement of the carbides is neglected: each carbide is considered to be located at the center of the unit cell. Furthermore, it is assumed that all elements remain homogeneously distributed in the ferritic matrix. Besides carbides, the unit cell contains one already nucleated cavity of radius a. Inside this cavity, the hydrogen pressure corresponds to the hydrogen pressure in the gas atmosphere to which the material is subjected (inside the reactor or autoclave). In this model the chemical reaction of carbon with hydrogen is assumed to occur rapidly so that the diffusion of the carbon atoms towards the cavity controls the kinetics of the methane formation.

As a result, the three submodels of the 1D model provide at each instant the change of the sizes of the carbides, the growth rate of the cavity and the number of newly formed methane molecules per unit of time. These rates allow us to update the composition of the ferrite and the methane pressure at each new time increment via an explicit time integration scheme.

MICROSTRUCTURAL MODEL

A second microstructural model is under development where, in contrast to the one-dimensional model, i) variations in spatial concentration can occur, ii) the spatial positions of the carbides are resolved and iii) methane formation is not per definiton purely diffusion controlled. The concept of this modelling is based on the variational methodology developed by Cocks and Gill [2] using the finite element technique. In its present state the microstructural model can handle interstitial (carbon) and substitutional (metal) diffusion in the ferritic finite elements and the chemical reaction to methane with the help of special surface reaction elements. The derivation of the governing equations and their discretization via shape functions is given in [3, 4]. The movements of carbide-ferrite interfaces can also be treated within the variational methodology. However, a simpler approach is used in the present code to incorporate the effect of carbides which allows to avoid higher computer times (for details see [4]). The outcome of the microstructural model are the distribution of the alloying elements, the sizes of the carbides and the methane pressure in a cavity of fixed size in dependance of the exposure time.

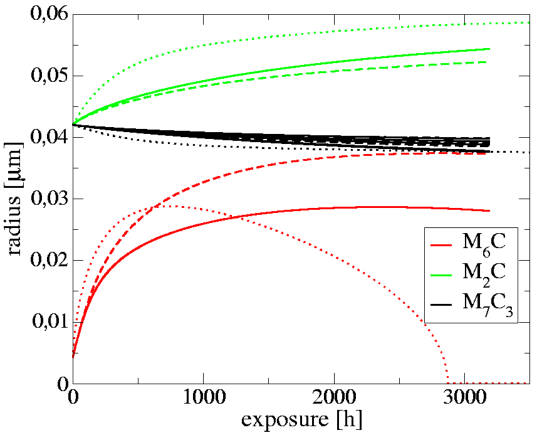

Figure 1. Carbide evolution of different carbides (black: 7 M_7C_3 carbides, red: 1 M_6C and green: 1 M_2C) during tempering at 570°C. Solid and dashed lines are the results of the microstructural model for two arrangements and the dotted lines refer to the results of the one-dimensional model.

RESULTS

In this paper the 1D model and the microstructural model are applied to simulate the microstructural evolution of the 2.25Cr1Mo steel during air exposure at 570°C. To limit the calculation time of the second model a relatively small two-dimensional sample is chosen. Nine carbides are distributed randomly in a ferrite: 7 M_7C_3 and 1 M_2C and a smaller M_6C carbide. Two different arrangements are investigated where the main difference lies in the distance between the Mo carbides M_2C and M_6C. In arrangement 1 they are nearer to each other than in arrangement 2. The predicted evolution curves of the carbide radii are potted in Fig. 1 as solid lines for arrangement 1 and as dashed lines for arrangement 2. Fig. 1 shows that M_2C grows while the M_7C_3 carbides shrink a bit. In arrangement 2 the M_6C carbide reaches a bigger size because, due to the larger distance, there is less interference between the Mo carbides. It holds for both carbide types that their driving force for growth increases with the Mo content of the ferrite. Consequently, these two carbide types compete for the Mo of the ferrite.

Additionally, the microstructural evolution obtained by the 1D model are shown as dotted lines (see Fig. 1). As the spatial arrangement is not taken into account in this simpler model and the ferrite composition is taken to be homogeneous, one just obtains a single curve per carbid type. The 1D model gives the same trend as the more sophisticated model, but the kinetics differ significantly. According to the 1D model M_2C grows faster because the impoverishment of Mo around the growing carbide is not resolved. The dissolution of the M_7C_3 carbides also goes slightly quicker in the 1D model. First the M_6C carbide grows but from 700h on its size shrinks while in the microstructural model it grows slowlier but reaches a larger size before shrinkage starts. As in the 1D model there is no spatial variation of the Mo-concentration, M_6C is directly affected by the M_2C carbide and vice versa. In the microstructural model the spatial variation of the alloying elements in the ferrite is resolved. Then, the substitutional diffusion determines the time until the carbides feel each other via the Mo concentration while the interaction between the carbides via the ferritic carbon concentration is present in both models from the beginning on.

Further results are available from the simulation of exposure tests in hydrogen.

CONCLUSIONS

In this paper two models are presented and applied to describe the microstructural evolution of carbides during tempering and exposure to hydrogen: i) a simple one-dimensional model and ii) a sophisticated microstructural model. Both are a multi-component, multi-phase continuum description of several processes involved in hydrogen attack.

References

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