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Mathematical modeling of residual stresses and distortions induced by gas nitriding of 32CrMoV13 steel

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The aim of this paper is to provide a model simulating the nitriding of 32CrMoV13 low alloy steels. The model is based on thermodynamics of irreversible processes and chemical kinetics. The mechanical approach is based on the mechanics of continuous media and considers an elasto-viscoplastic constitutive law. A self-consistent scale transition scheme establishes the link between chemical and mechanical calculations. The simulation describes the diffusion of nitrogen and carbon, the main precipitations with the associated volume changes, the residual stresses developed during treatment, and the distortions of complex structural parts. It enables evaluating the macroscopic volumetric eigenstrains, the thermal strain and the variation of Young's modulus induced by the treatment. The problem is solved by Finite Element calculations. The unknown inputs of the model are identified through an inverse method using different kinds of experimental data such as nitrogen and carbon mass fractions, distortions and residual stresses. Flat and cylindrical samples are employed for that purpose. These specimens are gas nitrided during 120 h at 550 °C. The simulation program is finally validated on a sample of complex geometry treated in the same conditions. The distortions predicted by the model are therefore compared to results of measurements carried out by 3D full-field optical scanning.

1. Introduction

Thermochemical treatments such as the nitriding process are commonly used in order to increase the fatigue life of structural parts [1,2]. In the aeronautic industry, the mass of the component is constantly reduced and leads to design parts with thinner walls. The small thickness of nitrided components affects their residual stress distribution and consequently increases their sensitivity to distortions. These deformations have to be mastered in order to ensure the conformity of treated parts.

The modeling of the nitriding process is complex because it involves multiple and coupled phenomena. The prediction of distortions generated by residual stresses requires a good knowledge of the stress–strain constitutive law for the studied material. In the case of the 32CrMoV13 low alloy steel, studied in this work, some consider an elasto-plastic behavior [3,4], others an elasto-viscoplastic one [5–7].

Furthermore, the prediction of residual stresses requires a good description of the diffusion and reaction phenomena, activated by the treatment temperature and controlled by the nitrogen concentration on the surface of the material. Indeed, it is established that residual stresses are generated by the incompatibility of volumetric eigenstrains induced by the precipitation of MN nitrides ($M = Cr, Mo, Va$) [6,8–10]. In the case of pure iron or iron–chromium and iron–vanadium alloys, several works intend to model the nitrogen diffusion-precipitation phenomena [11–18]. Fewer studies are available in the case of carbon iron-based alloys such as 32CrMoV13. Carbon plays an important role in the generation of residual stresses. Indeed, the dissolution of initial carbides releases carbon atoms then available for diffusion. They can diffuse in the depth or be evacuated from the steel, which involves decarburizing on the surface [19].

Finally, only few models are available to deduce the distortions of treated parts from the diffusion of nitrogen and carbon [5,7,20].

The aim of this work is therefore to provide a global multi-physics model of the gas nitriding process that accounts for most important diffusion and phase transformation mechanisms, and permits predicting both residual stresses and distortions of treated parts. However, due to the complexity of the phenomena involved in the nitriding process, some input parameters of the model are not found in the literature and cannot be evaluated by direct measurements.

Thus, this data will be identified by an inverse method whose cost function will incorporate different types of experimental

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measurements (nitrogen and carbon in-depth profiles measured by Glow Discharge Optical Emission Spectroscopy (GDOES), residual stresses evaluated by X-ray diffraction, and geometrical distortions characterized by optical measurements).

Additionally, the model will be implemented in a finite element code in order to predict residual stresses and distortions of complex parts. This approach will be validated on an industrial case study.

In this paper, we will focus on nitriding of 32CrMoV13 low alloy steel, treated 120 h at 550 °C.

2. Nitriding model

2.1. The initial material

Before nitriding, the studied steel goes through several thermal treatments that generate the precipitation of tempering carbides in a non-equilibrium carbon martensite phase that consists in a strained body centered quadratic structure supersaturated with interstitial carbon. Metallurgical analysis and thermodynamical computations performed on Thermo-Calc® software showed that $M_{23}C_6$, M_7C_3 et M_3C are the main initial carbides in the 32CrMoV13 before treatment [19,21]. Thermo-Calc software provides the types of formed precipitates and the distribution of the alloying elements (M = Cr, Mo, Va) into carbides. However, the martensitic structure is not considered because computations on Thermo-Calc are performed under the assumption of thermodynamic equilibrium. This hypothesis entails that the maximum quantity of carbon contained in an iron solid solution is limited to the carbon solubility in pure α iron, highly lower than in the martensite phase.

The analysis of X-ray diffraction peaks has enabled to evaluate the mean lattice parameters of martensite and its carbon fraction using methods defined by Sprauel and Michaud [22]. In the case of the 32CrMoV13 steel, a third ($\chi_C^{\alpha'} = 0.105\%$) of the total carbon mass fraction ($\chi_C^{tot} = 0.32\%$) is dissolved in the martensite whereas the rest is incorporated in carbides. After a material balance, it seems that the carbon is the limiting element for the formation of tempering carbides. Thus, the composition of the martensitic phase could be estimated.

During the nitriding process, the nitrided layer can be separated in two distinct zones (Fig. 1). The first one is the combination layer constituted of $\gamma' - Fe_4N$ and $\varepsilon - Fe_{2-3}N$ nitrides, widely studied for its good tribological properties [1,9,23]. The second one is the diffusion zone constituted of MN nitrides and carbides embedded in the martensitic matrix [19]. Because of its thinness (30 µm), the contribution of the combination layer to the global distortion of parts is assumed to be negligible in comparison to the deformation imposed by the diffusion zone (1 mm thickness). In fact, finite element simulations were performed for our samples of smallest thickness (3 mm). These calculations were carried out considering residual stress level of a few hundreds MPa in a combination layer of 30 µm thickness. This permitted to conclude that the stresses induced in the diffusion layer are negligible in comparison to the error bars of our experimental results. A similar conclusion was obtained for the distortions. For these reasons, the combination layer is not modeled.

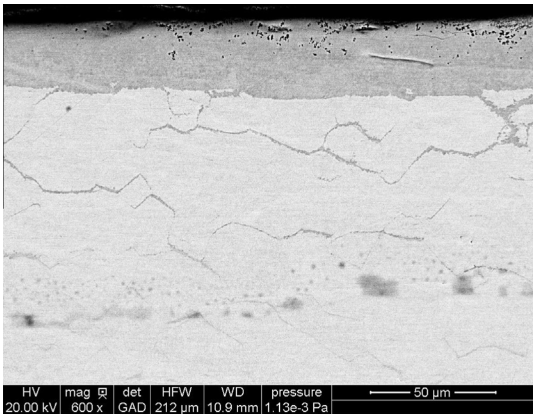

Fig. 1. XPS in-depth analysis of a nitrided layer. Gas nitriding at 550 °C during 120 h. The dark gray zone is the combination layer (thickness ≈ 30 µm), the lower zone, in pale gray, is the beginning of the diffusion zone (up to 1 mm in-depth).

2.2. Reactions of precipitation

Many precipitations take place in the diffusion zone. Only the most influent on the development of residual stress are selected (Eq. (2)). All reactions are considered stable and stoichiometric. The order of magnitude of the precipitation equilibrium constants, as derived from the standard reaction enthalpies, shows that reactions (2.1–7, 9 and 11) are total ($K_{eq} > 10^4$), whereas the recarburizing and the formation of cementite (2.8–10) are not ($K_{eq} < 10^4$). However, because of their low quantity, all reactants are rapidly transformed before reaching a potential equilibrium. For this reason, all reactions are assumed to be total, hence the selected precipitation kinetics (Eq. (3)).

The first two reactions (2.1–2) represent the precipitation of semi-coherent nitrides formed from the alloying elements in the iron solid solution [21]. Chromium and molybdenum are selected for their strong affinity with nitrogen [24,25].

Reactions (2.3) and (2.5) correspond to the formation of incoherent nitrides after dissolution of the initial $M_{23}C_6$ and M_7C_3 carbides aggregated in the former grain boundaries. After dissolution, the carbon initially contained in the carbides is released to diffuse in solid solution.

Reactions (2.4) and (2.6) describe the formation of incoherent nitrides after dissolution of the new Mn_7C_3 and M'_7C3 carbides, themselves generated by reactions (2.8) and (2.9). The latter are activated by the presence of the diffusing carbon released by reactions (2.3–7).

Reaction (2.7) represents the formation of nitrogen martensite. Indeed, the analysis of the lattice parameter of the matrix by using X-ray diffraction has shown a nitrogen mass fraction in martensite ($\chi_N^{\alpha'} = 0.146\%$) in the decarburized zone (50 µm < z < 100 µm in depth).

Thus, it is assumed that the carbon inserted in the initial martensitic lattice is progressively ejected and replaced by nitrogen during the treatment. The overall structure of the phase is however preserved, thus forming nitrogen martensite. In the mechanical approach, the mixed carbon and nitrogen martensite matrix is nevertheless taken as one constituent.

These assumptions lead to consider that the excess nitrogen consistently observed in this type of steel [15,16] is not only concentrated around the semi-coherent nitrides, but is also contained in a nitrogen martensite structure.

Thus, most nitrogen and carbon of the iron base matrix is considered to be inserted in the martensite crystal lattice, and only a part of these elements is available for diffusion along grain boundaries, martensite lath boundaries and dislocations. The sum of interstitials and diffusing atoms both contained in the martensite should however not exceeds its solubility. A maximum concentration criterion of species is therefore considered as follows:

$$C_{N^{\alpha'}} + C_N + \frac{r_N}{r_C}\left(C_{C^{\alpha'}} + C_C\right) \leqslant C_N^{max} \quad (1)$$

where $C_{N^{\alpha'}}$ and $C_{C^{\alpha'}}$ are the molar concentrations (mol/m³) of interstitial nitrogen and carbon of the martensite. C_N and C_C are the