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Precipitation of aluminum nitride in a high strength maraging steel with low nitrogen content

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ABSTRACT

In the present work, aluminum nitride (AlN) precipitation was investigated in a X23NiCoCrMoAl13-6-3 maraging steel with low nitrogen content (wt.% N = 5.5 ppm). A reliable and robust automatic method by scanning electron microscopy observations coupled with energy dispersive X-ray spectroscopy was developed for the quantification of AlN precipitates. The first stage was to identify the solvus temperature and to develop a heat treatment able to dissolve the AlN precipitates. The experimental determination of equilibrium conditions and solvus temperature show good agreement with ThermoCalc® simulation. Then, from this AlN-free state, the cooling rate, isothermal holding time and temperature were the subject of an intensive investigation in the austenite region of this maraging steel. In spite of the high temperatures used during heat treatments, the growth kinetic of the largest AlN precipitates (>1 μm) is slow. The cooling rate has a major effect on the size and the number density of AlN due to a higher driving force for nucleation at low temperatures. At last, quenching prior to isothermal annealing at high temperatures leads to fine and dense AlN precipitation, resulting from the martensite to austenite transformation. Experimental results will be discussed and compared with kinetic data obtained with the mobility database MobFe2 implemented in Dictra® software.

1. Introduction

At a time when kerosene costs more and more, airlines are seeking to minimize fuel consumption, and aircraft and engine manufacturers are putting strong efforts to develop competitive solutions for this purpose. Concerning the turbofan engines, one of the most efficient ways to realize this goal is to increase the bypass ratio, and to increase the torque transmitted from the turbine to the fan by the driveshaft. This can be done by improving the mechanical properties of the current materials used for the turbine shaft. To this end, new maraging steels have been developed and patented. Their improved mechanical properties are coming not only from the aging of martensite, but also from the hardening induced by the co-precipitation of the intermetallic phase, B2-NiAl, and the secondary carbides M_2C [1]. Since, nitrogen cannot be completely avoided in these maraging steels using current melting technologies such as VIM (Vacuum Induction Melting) or VAR (Vacuum Arc Melting), precipitation of nitrides may occur during solidification and/or heat treatment [2]. When the material is subjected to cyclic loading, several fracture surfaces of test pieces showed that cracking is initiated on AlN precipitates with a large size. These large precipitates affect the fatigue lifetime of any parts subjected to cyclic loading, particularly the driveshafts. Thus, one way of improvement of the fatigue lifetime goes through size reduction of these AlN precipitates. The aim of this paper is to meet this challenge.

When the alloy contains aluminum, combined with the lack of titanium or niobium, AlN precipitation occurs in the austenitic or ferritic regions. Several investigations report a fine precipitation (≪1 μm) with a high number density of nitride particles for steels containing between 30 ppm and 300 ppm nitrogen [3]. This precipitation is known to have significant effects upon recrystallization and austenite grain growth [4]. The austenite grain size directly affects the mechanical and technological properties including hot ductility and deep drawability [5,6]. Although aluminum nitrides are beneficial in restricting grain growth, they can cause embrittlement and induce cracking phenomena such as rock candy fracture during continuous casting and hot rolling [7–9]. Depending on the Al and N content as well as the thermomechanical processing route, AlN precipitates can adopt various morphologies: cuboids, rods, large plates or spherical particles. A summary of the different morphologies of AlN in steels was made by Wilson and Gladman [10]. From a crystallographic point of view, most authors report a hexagonal structure for the AlN precipitates. However, Massardier et al. [11] observed that the precipitation sequence can be more complex. Indeed, in the early stage of precipitation for low carbon aluminum-killed steel, the precipitation seems to start from a cluster of chromium atoms

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with a metastable face-centered-cubic phase, which tends towards equilibrium hexagonal structure. In the case of Fe–Al–N alloy, Sennour et al. [12] also identified a face-centered-cubic — hexagonal transformation of AlN precipitates via a Shockley mechanism. This transformation is activated by heterogeneous nucleation on iron sulfide.

The precipitation of AlN during isothermal heat treatment applied after a solution treatment follows the classical C-curve behavior. It has been shown that the $\gamma \rightarrow \gamma + \alpha$ transformation in isothermal conditions accelerates the precipitation kinetics of AlN [6,13–15], due to a lower solubility of nitrogen in the ferrite. In the austenitic region, the precipitation occurs predominantly at grain boundaries because of considerable volumetric misfit between the AlN precipitate and the steel matrix [16] and an increase of the diffusivities of elements at the grain boundaries as compared to grains [3]. Extensive experimental and modeling works about AlN precipitation kinetic are reported in the literature [16–18]. The most detailed studies are due to Radis et al. [3,19,20]. Based on the nucleation/growth model, these authors have computed the precipitation kinetics of AlN in various alloys. Compared to available results from the literature, the latter simulations clearly indicate that AlN precipitation occurs both at grain boundaries and dislocations. Furthermore, it has been shown that the precipitation kinetics are highly dependent not only on the chemical composition in nitrogen and aluminum, but also on the grain size and annealing temperature.

In the present work, the AlN precipitation kinetics has been studied in a maraging steel with a low nitrogen content. Heat treatments were conducted in isothermal condition starting from an AlN-free state. In addition, the effects of cooling and heating rates have been studied from this nitrides-free microstructure. The evolution of size distribution and number density will be the subject of special attention. The obtained results will be compared with equilibrium (ThermoCalc®) and discussed with kinetic data (Dictra®).

2. Material and experimental procedure

2.1. Material and heat treatments

In the present study, the ML340™ maraging steel, whose nomenclature in the European standard is: X23NiCoCrMoAl13-6-3, was supplied by Aubert & Duval (Eramet Group). The chemical composition of this steel is given in Table 1. Several heat and thermomechanical treatments were carried out on the ingot, ensuring that the initial dendritic microstructure was transformed into homogeneous bulk material. After forging, the billet (Ø 250 mm) was normalized and softened. This state will be hereafter labeled the as-received state.

Cubic specimens, with a dimension of $20 \times 20 \times 20$ mm^3, were machined from the as-received state prior to further heat treatments. In order to limit chemical and structural segregations, the samples were extracted from the vicinity of the billet's half-radius. The specimens were placed in an inert atmosphere with argon gas flow. The temperature was measured with an S-thermocouple, located close to the specimen, and controlled in real time with a numerical PID regulator. Many heat treatment conditions were chosen to demonstrate the effects of cooling rate, isothermal holding time and isothermal holding temperature on the AlN precipitate formation. Additional heat treatments were conducted to determine the equilibrium state as a function of the temperature, in particular the temperature stability range of occurrence of AlN precipitates. The heat treatment conditions will be detailed hereinafter.

2.2. Crystallography, morphology and chemical composition

X-ray diffraction (XRD) diagrams were recorded from the as-received state using either high energy X-ray synchrotron diffraction at the ESRF (European Synchrotron Radiation Facility) in Grenoble, France, on the ID15B beam-line with a wavelength of 0.14264 Å (for a review on experimental procedure, see [21]) or a conventional diffractometer with Cu-$K_{\alpha 1}$ radiation ($\lambda_{Cu\text{-}K\alpha 1} = 0.154056$ nm), with the power fixed at 1600 W (40 kV and 40 mA). The conventional instrument was set up for Bragg–Brentano geometry with a line focus and a Ge (111) monochromator in incident beam arm. As the volume fraction of the AlN precipitates is low (typically $7.4.10^{-3}$% in the as-received state), the precipitates were extracted from the as received state for conventional X-ray characterization. A modified Berzelius solution at room temperature [22] was used for chemical dissolution of the matrix. After complete dissolution of the matrix, a Bioblock Sigma 6–15 centrifuge was used to separate powder particles from the acid solution. The centrifuging process was repeated 3 times to clean the residues. Finally, residual powder was recovered after drying out at 80 °C for 12 h. After selective chemical dissolution, the AlN precipitates shape was analyzed using Scanning Electron Microscope (SEM-Quanta FEI 600) in secondary electron (SE) and backscatter electron (BSE) modes. For microstructural investigation by Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED), the thin foil was prepared using a Focused Ion Beam (FIB) system. The sample for TEM and HRTEM (High Resolution TEM) was investigated using JEOL ARM 200 F Cold FEG, operating at an accelerating voltage of 200 kV, and equipped with a GIF Quantum ER model 965 for EELS (Electron Energy Loss Spectroscopy) analysis. Quantitative EELS analysis was achieved by the classical inner-shell ionization edge data processing. Thus, the atomic concentration ratio $C_{A/B}$ of any element A and B may be evaluated from the spectrum using the following relation [23]:

$$C_{A/B} = \frac{I_A(\Delta)}{I_B(\Delta)} \frac{\sigma_B(\beta,\Delta)}{\sigma_A(\beta,\Delta)}$$

where $I_i(\Delta)$ is the characteristic-loss signal in spectra usually measured as the area integrated over an energy range Δ beyond the corresponding edge after background removal by inverse power law, and $\sigma_i(\beta,\Delta)$ the partial cross-section (by using Hartree–Slater model [24]) within an acceptance angle β and an energy window Δ.

Table 1
Chemical composition (wt. %) of ML340™ steel.

Fe	Ni	C	Co	Cr	Mo	V	Al	N
Bal.	13.1	0.23	5.9	3.25	1.6	0.24	1.43	5.5 ppm

2.3. Microstructural features by image analysis

As the mass fraction of AlN is expected to be very low due to the low nitrogen content in the steel (5.5 ppm), a large number of images has to be acquired to ensure a statistically significant study. The minimal surface required is estimated to be 15 mm^2, which corresponds to about 400 backscattered scanning electron microscopy (BSE-SEM) images at the chosen magnification (×500). Consequently, a reliable and robust method for the quantification of AlN precipitates was developed. With the help of software specifically developed for particle analysis, the sample stage can be driven and the sample completely analyzed automatically. When a particle is detected, the algorithm finds its center and takes a second image with an increased magnification. Then, two criteria must be satisfied for a particle to be defined as AlN precipitate. First of all, the minimum Feret diameter must be greater than 0.5 μm and secondly the particle must contain aluminum and nitrogen. Because X-ray is not only emitted by the particles itself but also by the surrounding steel matrix, the particles containing more than 3 at.% nitrogen and more than 8 at.% aluminum are considered as AlN precipitates. When both criteria are satisfied, the spatial coordinates, mean equivalent diameter and surface fraction are determined by image analysis.