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Vanadium Carbide Dissolution During Austenitisation of A Model Microalloyed FeCV Steel

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Abstract. High performance commercial micro alloyed steels contain elements such as vanadium, which leads to a fine dispersion of vanadium carbide precipitates. The precipitation state, in terms of volume fraction and size distribution, plays a significant role in final mechanical properties of the material. Different austenitisation heat treatments were performed on a model ternary alloy FeCV. Precipitation states were characterised combining different experimental techniques. TEM was used to identify the chemical composition of observed precipitates. ICP mass spectroscopy was performed to measure the volume fraction of precipitates. The size distribution was studied by SEM. Results are characteristic of a coarsening regime.

Introduction

It is well known that vanadium has a strong affinity for carbon and that a small addition of this element to steels yields a significant improvement of mechanical properties. Indeed, addition of vanadium leads to a microstructure formed of a fine dispersion of vanadium carbide precipitates in α ferrite [1-3]. These precipitates contribute to the improvement of mechanical properties by precipitation strengthening [1,3,4] and by grain size control during austenite-ferrite transformation (refinement of ferrite grain size) [1,3-5]. The control of the precipitation state (e.g. the main characteristics of the precipitates, such as size distribution and volume fraction) plays an extremely important role in improving the overall property of steels. Hence, a detailed characterisation is necessary for the optimisation of mechanical properties.

During steel fabrication and shaping processes, different heat treatments are performed. Some of these are performed in austenite phase. Several works have been published to understand precipitation phenomena in High-Strength Low-Alloy (HSLA) steel [2,4-10]. However, to the authors' knowledge fewer works about the precipitation/dissolution phenomenon of carbides within the austenite phase have been reported.

Different experimental techniques are used to characterise the microstructure and the precipitates in steels. Transmission Electron Microscopy (TEM) appears as one of the most widely used for this purpose [2,4-7,10,11]. Indeed, TEM combined with other associated techniques is a powerful tool for the imaging of secondary phases in steel, especially in the early stages of precipitation. Craven et al. have shown that it is feasible to study vanadium carbides precipitates, even close to nucleation using Electron Energy Loss Spectroscopy [10,12]. Energy Filtering TEM has also been shown to be a good technique for precipitates characterisation [13,14].

This paper reports experimental results of the characterisation of vanadium carbide precipitates in a model ternary alloy FeCV, after different heat treatments in austenite phase. Various characterisation techniques (including SEM and TEM) were used to obtain the chemical composition, the volume fraction, and the size distribution of these precipitates. Results presented in this paper are part of a work aiming to model the microstructure evolution of commercial steels containing vanadium and niobium during austenitisation heat treatments.

Materials and Experimental Procedure

Model Alloy. A high purity model alloy, FeCV, was used for experimental investigation of the microstructure and composition of vanadium carbides after different dissolution treatments. The composition of this alloy is 0.5 ± 0.01 wt% of carbon and 0.2 ± 0.01 wt% of vanadium. Other elements are present in individual quantities less than 5 ppm. This model alloy was elaborated by the MHP group at the E.N.S.M., Saint Etienne, France.

The alloy was solution treated at 1000°C for 30 minutes and water quenched to room temperature. In order to study the dissolution of carbides, a heat treatment was designed to precipitate almost all the vanadium and obtain precipitate radii as large as possible. For that purpose, specimens were heated at 700°C for 10 h (nucleation and growth in ferrite) in vacuum (quartz encapsulation), then they were heated at 800°C for 10 days (coarsening in austenite), and finally slowly cooled down to room temperature. This state (called *Fully Precipitated State* (*FPS*)), was chosen as the starting point for a series of isothermal heat-treatments (reversion) in austenite. Reversion experiments were performed in a molten salt bath. *FPS* samples were treated at 870°C and 920°C for 2, 5, 10, 20, and 60 min. After reversion treatment, samples were water quenched to room temperature. These states will be here after called as *Partially Dissolved States* (*PDS*).

Experimental Procedure. Structural characterisation of carbides was made by TEM with a microscope equipped with a field emission gun (2010F from JEOL). Precipitates were examined using imaging techniques, electron diffraction, and EDX with an OXFORD-Inca analyser. Thin foils were prepared by mechanical polishing to a final thickness of 20-30 µm (in order to minimize the magnetic effects during observation), followed by an argon ion beam thinning process in a Polishing Precision System (PIPS) from GATAN.

The measurement of the quantity of precipitated vanadium has been performed by dosing the precipitated phases after an electrolytic dissolution. The matrix was dissolved by controlled electrolytic dissolution. Precipitates were collected by filtering the electrolyte, and they were further dissolved in a controlled solution. This solution was analysed by Inductive Coupled Plasma (ICP) spectroscopy giving the quantity of vanadium in precipitates.

Finally, Scanning Electron Microscopy (SEM) analysis was carried out with a Field Emission Gun (FEG) environmental scanning electron microscope XL30 from FEI in the high vacuum mode. Samples were cut into 10x5x1 mm^3 blocks, then polished to ¼ µm finish with diamond paste. The polished surface was etched in either 4 % or 0.4 % Nital during 5 to 10 s to reveal precipitates just before examining the samples in the microscope.

Results and Discussion

Identification and Structural Characterisation of Precipitates. High resolution SEM images were obtained using secondary electrons for all the samples. The micrographs show quasi spherical particles either for the *FPS* or *PDS* samples (figure 1). Observed particles have diameters ranging from 30 to 150 nm.

SEM does not allow us to precisely identify neither the crystallographic nature nor the chemistry of the observed particles. Hence, a parallel study was carried out on these samples using TEM to confirm the nature of the precipitates.

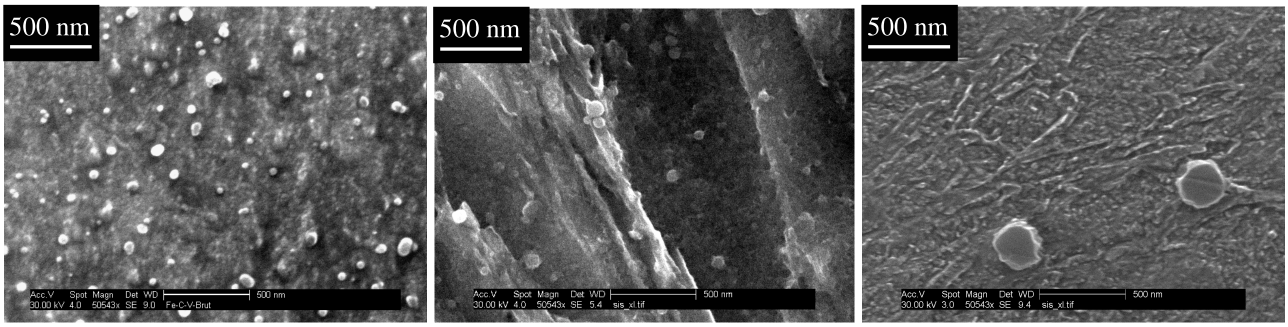


Figure 1. SEM micrographs at high magnification (x 50000) showing vanadium carbide particles for different states: a) *Fully Precipitated State;* b) 870°C 10 min; c) 920°C 5 min

TEM Micrographs of the *FPS* showed a ferrito-pearlitic matrix (figure 2 (a)). Observations were performed mainly in ferrite α grains. Typically spherical particles were observed with an average diameter of about 60 nm (see figure 2 (b)). Presence of vanadium in the particles was systematically confirmed by EDX analysis. To identify the structure of the observed particles Electron Diffraction (ED) patterns were recorded from several precipitates. Figure 2 (c) shows the typical ED pattern of a particle in a [1-1-1] ferrite grain. This diagram identifies unambiguously the V_6C_5 long-range ordered form reported in [15] (monoclinic B2/m, with a = 0.509 nm, b = 1.018 nm, c = 0.882 nm and $\gamma = 109.47°$). This compound has already been identified by micro-diffraction in a low alloy steel [7] and in cast iron [16].

However, in many cases ED patterns did not show superlattice reflections, and were then consistent with the stoechiometric vanadium monocarbide VC structure (fcc NaCl type, a = 0.417 nm). Indeed, discerning the ordered and disordered forms of vanadium monocarbide requires an accurate exploration of the reciprocal lattice, which in general appears to be almost impossible, owing to the magnetism of the thin foils.

It should further be mentioned that all observed particles did not show any orientation relationship with the ferritic matrix; they are indeed incoherent with the matrix because their classical Baker-Nutting orientation relationship [17] has been lost, following the ferrite-austenite transformation during the heat treatment at 800°C.

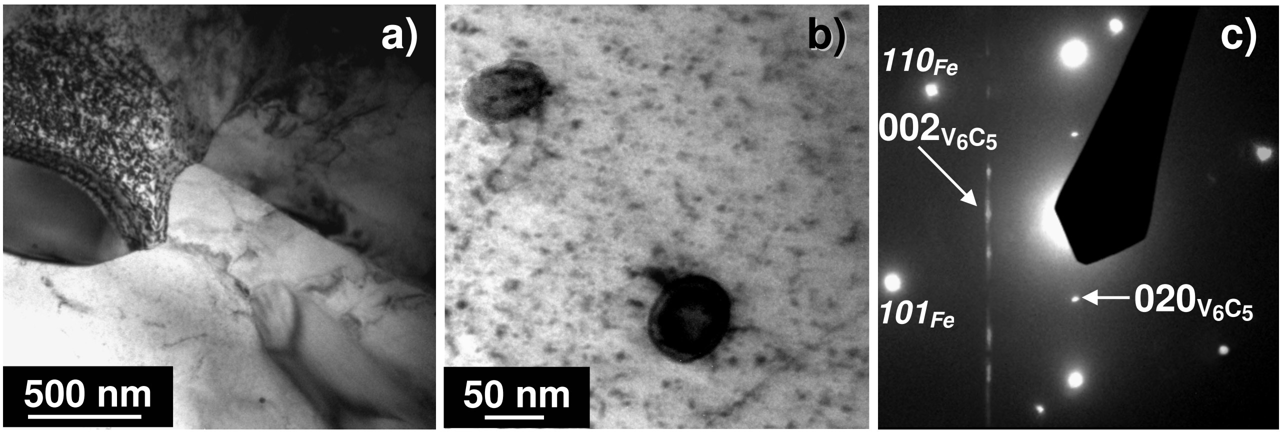


Figure 2: TEM microstructure of the *Fully Precipitated State:* a) low magnification image of the ferrito-pearlitic matrix; b) quasi-spherical vanadium carbide precipitates; c) Electron Diffraction pattern in the $[1\text{-}1\text{-}1]_{Fe}$ matrix orientation showing the $[100]_{V_6C_5}$ lattice section (according to the monoclinic form reported in the text) of a precipitate.

All *PDS* exhibit a complex martensitic microstructure. Because of the reversion treatment and the quenching, it is more difficult to observe particles in dissolved states than in *FPS*. Figure 3 shows different bright field TEM micrographs of carbides for the sample heat treated at 870°C for 2 min. Typically, particles observed are quasi-spherical and have a larger scatter in the size than those observed in *FPS*; with a diameter ranging from 20 to 100 nm. However, bigger particles (of about 150 nm of diameter) could also be detected.

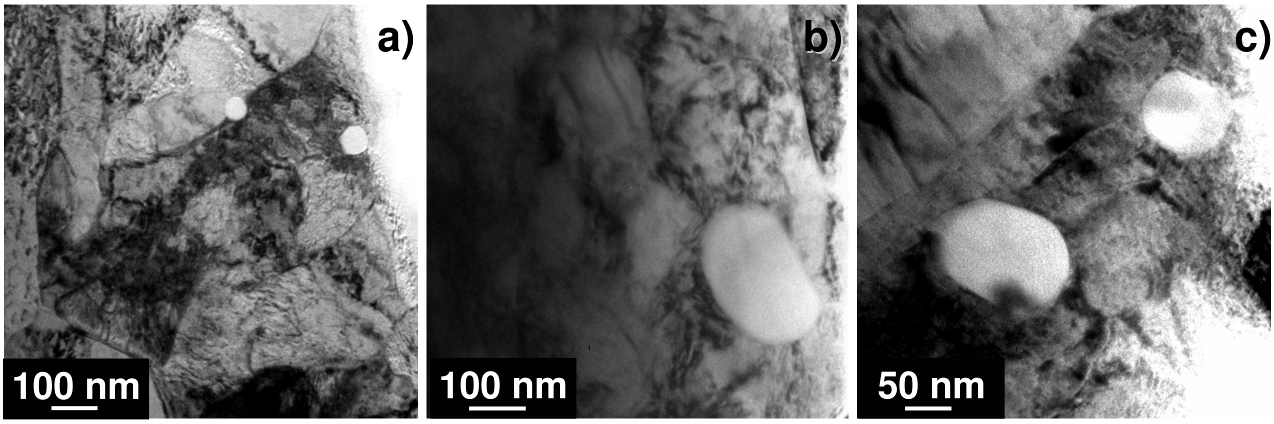


Figure 3: TEM microstructure of the sample heat-treated at 870°C for 2 minutes: a) low magnification image of the martensitic matrix; b-c) quasi-spherical vanadium carbide precipitates.

Again, presence of vanadium is systematically confirmed by EDX analysis. ED work shows that all precipitates were at least consistent with the known fcc structure of stoechiometric vanadium monocarbide, most of them being positively identified as the long-range ordered V_6C_5 phase.

The microscopic study coupling SEM and TEM has confirmed that spherical vanadium carbide particles can be clearly observed by high resolution SEM. However TEM remains necessary for the precise composition analysis and crystallographic characterization; further work is being done to identify precisely the nature of the particles in all the heat treated samples using extraction replicas.

Evaluation of the Volume Fraction of Precipitates. ICP mass spectroscopy after electrolytic dissolution gives the weight fraction of precipitated vanadium. Figure 4 shows the evolution of this value with the time of heat treatment for both dissolution temperatures, 870°C and 920°C. Measures have been done at least twice for each dissolution state. The profile of the evolution is characteristic of a thermally activated dissolution phenomenon. Weight fraction of precipitated vanadium decreases with treatment time; the higher the dissolution temperature is, the faster this diminution occurs. Furthermore, values of the equilibrium weight fraction obtained by thermodynamical calculations (Thermocalc [18]) are reported in figure 4. The weight fraction of precipitated vanadium measured in the *FPS* is in reasonable agreement with the equilibrium value at 800°C, and experimental measurements show that equilibrium is almost reached after 1 hour at 870°C and 1 hour at 920°C.

Precipitate volume fraction is a key parameter to characterise a precipitation state. It can be obtained from electrolytic dissolution results: indeed volume fraction of precipitates is linked to weight fraction of vanadium precipitated by the following relation:

$$f_{vol}^{VC}(T,t) = f_m^V(T,t) \cdot \frac{\rho_{Fe}}{\rho_{VC}} \cdot \left(\frac{M_C}{M_V} + 1 \right) \tag{1}$$

Where ρ_{Fe} is the density of iron, ρ_{VC} is the density of a VC carbide, M_C and M_V are the molar masses of carbon and vanadium, respectively. This equation assumes that all carbides have the fcc stoechiometric structure of VC; however, if all the observed particles were V_6C_5 carbides, this would lead to an absolute error less than 0.02 %. It also assumes that the density of the alloy is equal to the density of pure iron, which is quite reasonable considering that the volume fraction of precipitates is lower than 0.4 % in the *FPS*.

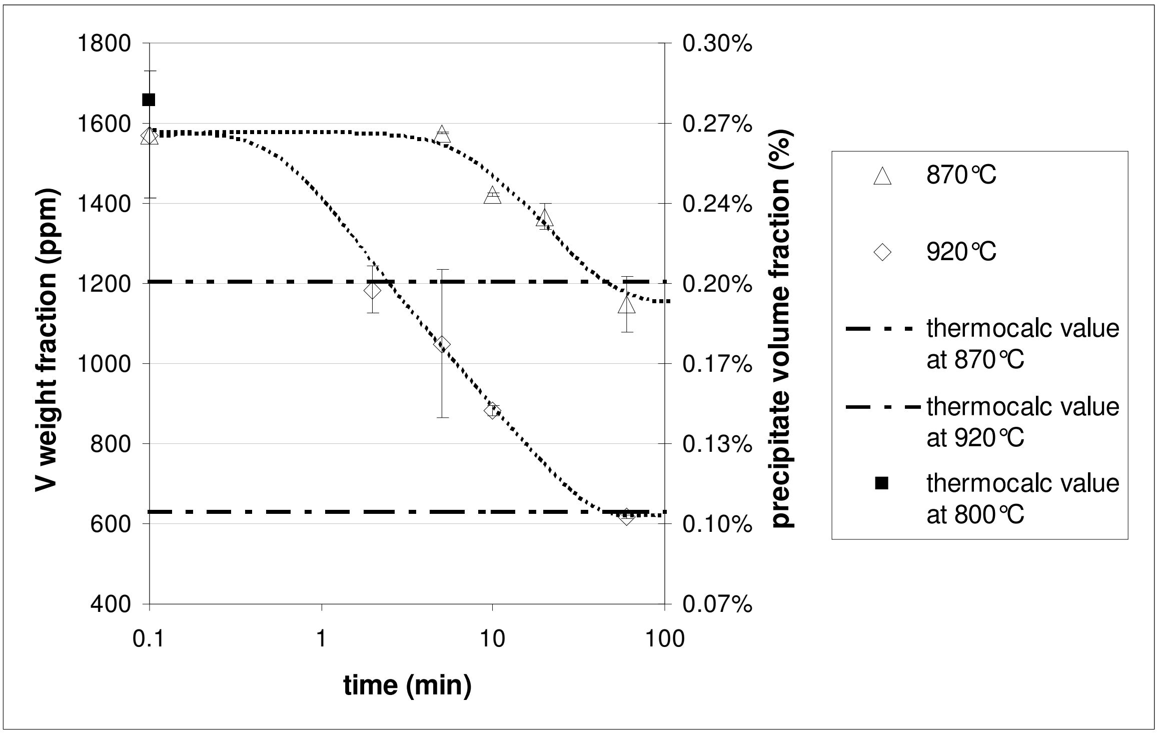
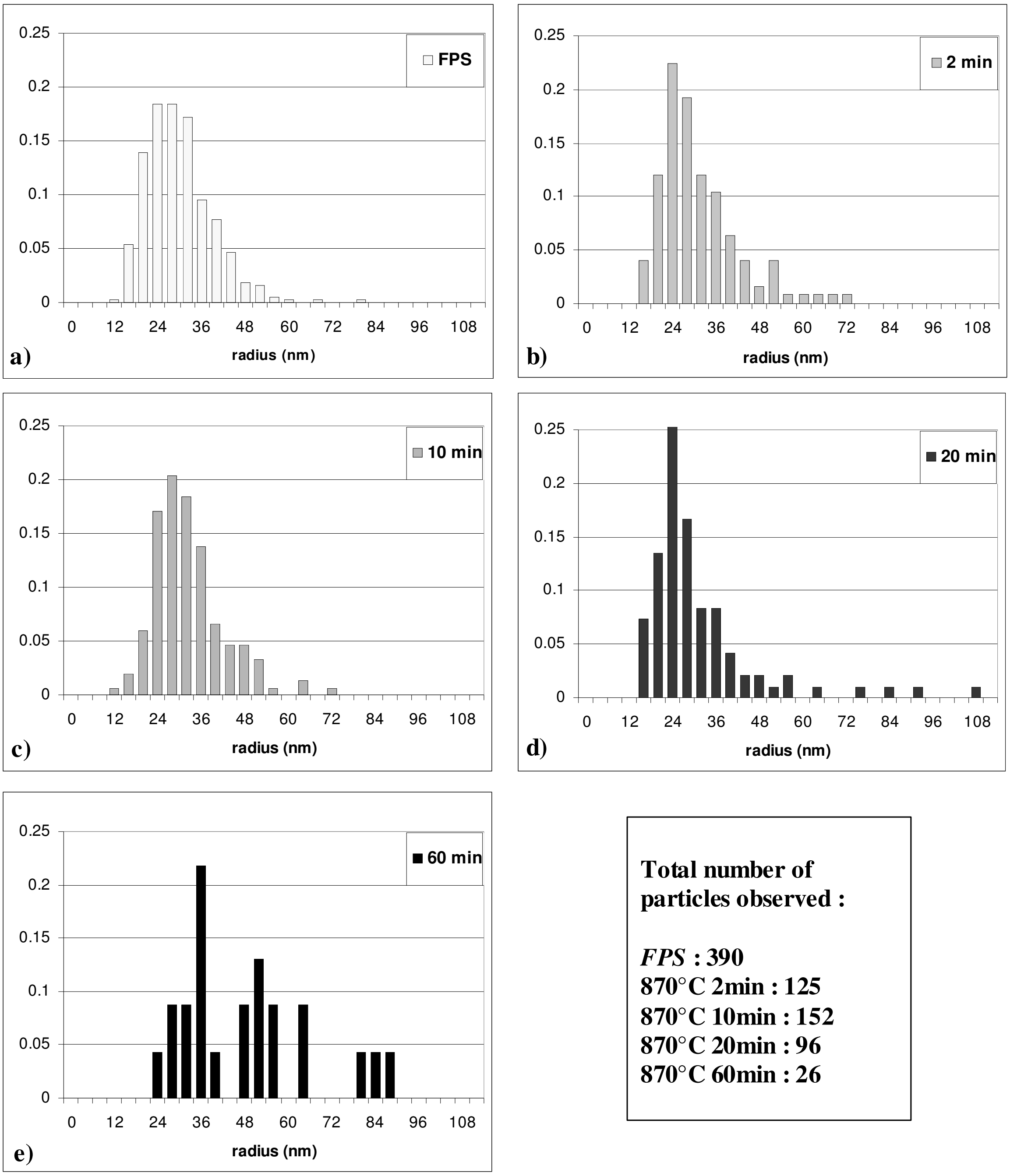


Figure 4. Evolution of the weight fraction of precipitated vanadium during heat treatments in austenite phase.

Further work is in progress to estimate the volume fraction of precipitates from an other approach, i.e. image analysis of SEM micrographs. Preliminary results show that a correct order of magnitude is obtained under reasonable assumptions for the geometry of the etched sample.

Study of the Size Distribution. Image analysis of SEM micrographs gives apparent diameter of observed particles. Thus a statistical study of size distributions can be performed. A preliminary study has been done on 15 micrographs for each state (*FPS* and *PDS*). It allows the validation of the technique and shows the effect of dissolution heat treatments on size distribution.

Figure 5 (a) shows the size distribution obtained for 390 particles observed in the *FPS*. The average radius of particles is of 28 nm. And the most frequent size classes are between 24 and 32 nm. Characterisation of this state is particularly important because it is the starting point for dissolution treatments.



Total number of particles observed :

FPS **: 390**
870°C 2min : 125
870°C 10min : 152
870°C 20min : 96
870°C 60min : 26

Figure 5. Evolution of size distribution of vanadium carbides precipitates during heat treatment in austenite phase at 870°C: a) *Fully Precipitated State* (*FPS*); b) 2 min; c) 10 min; d) 20 min; and e) 60 min.

The same work was done for *PDS*. Figures 5 (b), (c), (d), and (e) exhibit the size distribution obtained and the number of particles observed for states heat treated at 870°C for 2, 10, 20, and 60 min. All distributions have the same shape even if the number of observed particles is low for the last *PDS* (figure 5 (e)). Table 1 reports the average radius of the precipitates for the heat treatments considered in figure 5; it can be seen that the average size increases with increasing heat treatment time. This occurs both through dissolution of smaller particles, and growth of larger ones (see figure 5 (e)), which is consistent with a coarsening regime.

Table 1. Mean radii for the *Fully Precipitated State* (*FPS*) the *Partially Dissolved States* treated at 870°C.

Time of treatment [min]	0 (*FPS*)	2	10	20	60
R [nm]	28 ± 1	29 ± 1	30 ± 1	29 ± 1	46 ± 2

Conclusion

Different heat treatments in austenite phase were performed on a *Fully Precipitated State* (FPS) of a model low alloy FeCV. Vanadium carbide precipitates were characterised for each precipitation state.

(1) Combining three experimental techniques gives access to the characterisation of precipitation state:
   - Crystallo-chemistry of carbides can be obtained from TEM and ED work
   - Precipitate volume fraction is evaluated by ICP mass spectroscopy
   - Size distribution is measured from analysis of SEM micrographs.

(2) Reversion treatments performed in the austenite phase exhibit:
   - decreasing volume fraction with time
   - increasing mean radius with time

However, complementary work is still in progress, in order to obtain a statistical analysis grounded on the observation of a larger number of particles.

Results presented in this paper are very useful experimental data to calibrate a precipitation/dissolution model devoted to ternary alloy FeCV. The present approach will also be extended to more complex quaternary alloys in a near future.

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