Microstructural evolution of 9Cr–1Mo steel during long term exposure at 550°C

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Abstract

Thermal exposure changes in the microstructure of the 9Cr-1Mo steel, largely used in thermal power plants and petro-chemical industry, have been investigated, through long term experience at 550°C in furnace, up to 7000 hours.

Detailed analysis of the microstructural evolution and changes in secondary carbides ($M_{23}C_6$) were carried out through SEM, XRD and EDX analysis. Electrochemical extractions were done because of the small volume of carbides. A progressive restoration of the tempered martensite matrix was observed. Moreover, a continuous increase of $M_{23}C_6$ size is revealed until stabilization after about 5000 hours of exposure. The nucleation of Laves phases is here found ; two inverse contributions may be concluded. When nucleating far from secondary precipitates, these phases grow by consuming matrix elements, which can trigger creep damages. Nevertheless, by surrounding the $M_{23}C_6$ carbides like a shell, Laves phases can slow down their growth and so contribute in solid solution hardening. X-ray diffraction analysis lead to determine the temperature-time dependence of the matrix and $M_{23}C_6$ lattice parameter.

I. Introduction

The 9%Cr high resistant steels, especially the modified 9Cr-1Mo steel, have proved good performances in thermal power plants, petrochemical industries and nuclear reactors since the eighties. These performances can be traduced by the high creep strength, the resistance to oxidation cracking and the adequate cost [1; 2].

The improved properties of this material is due to a tempered martensitic microstructure, rich in MX primary precipitates obtained after austenitization (where M=V/Nb and X=C/N) and $M_{23}C_6$ secondary carbides (where M is Cr, Fe, Mo or Mn) [3; 4].

The long term ageing enhance microstructural changes such as the coarsening of carbides, precipitation of new phases and segregation of some alloying elements at PAGBs (prior austenitic grain boundaries). The segregation occurs mainly at PAGBs than within martensitic laths, and can be reduced by adopting suitable heat treatments, but can not be completely avoided after long term exposure. The changes in the tempered martensitic matrix are enhanced by the coarsening of the finely distributed precipitates along boundaries mixed with coalescence and diffusion from original state. such a coarsening may be explained by an absorption of matrix elements [5; 6].

Element	Content	Standards
Fe	88.61	—
C	0.13	0.07-0.14
Cr	8,73	8-9.5
V	0,178	0,18-0,25
Mo	1,01	0.85-1.05
Ni	0.26	up to 0.4
Si	0,26	0,2-0,5
Al	0.015	up to 0.05
Co	0.01	—
Nb	0,112	0.02-0.1
Ti	0 ,005	—
W	0,015	up to 0.02
Pb	0,023	—
Mn	0.39	0.3-0.6

Table 1: *chemical composition of the as received tube compared to ASTM standards [8]*

The comprehension of the chemical and microstructural changes in the 9Cr-1Mo steel during thermal ageing is compulsory in order to evaluate its stability and performances in advanced industrial applications. In this work, there is an emphasis on the study of the size and chemistry evolution of secondary phases, the attempt is to establish correlations with results of investigations and empiric laws. At isothermal condition, the diffusion of alloying element can be analysed using the famous Johnson-Mehl-Avrami (JMA) transformation equation, in order to compare the kinetics data of solid-state [7].

II. Experimental

i. Materials

The chemical composition of the investigated material, in the as received state, is shown in table 1. Portions of 20x10x8mm cut from this material are exposed in furnace, at a temperature of 550°C, for different durations up to 7000 hours.

ii. Electrochemical extractions

For each sample, electrochemical extractions have been done to separate precipitates from the matrix, in order to be analysed using DRX. In this work, the working electrode is the T91 sample, the Ag/AgCl is choose as reference electrode, while the graphite serves as counter-electrode. The voltage is set around 2V. The electrochemical time vary from 4 to 5 hours. After chemical extraction, the sample is put in a solution of methanol, in an ultrasonic bath. Finally, the residue is recovered on a filter ; here a vacuum pump is used to suck the liquid.

iii. Techniques of analysis

Investigations are conducted using the following experimental techniques: Light Optical Microscopy (LOM), microhardness measurements, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX).

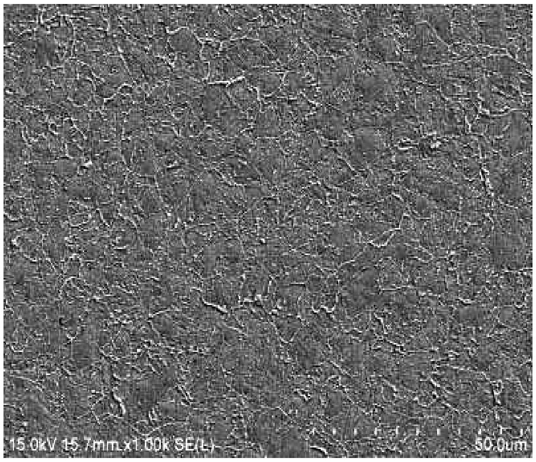
III. Results and Comments

The investigated material is consisted of a tempered martensitic matrix with of hardness value of 224H_v. The precipitates are finely distributed at PAGBs, subgrains and within martensitic laths (Fig.1a). After thermal ageing, clear changes are observed. Starting with coarsening (Figs. 1b and 1c), the tendency of precipitates is a continuous diffusion and coalescence to form relatively huge carbides (Fig.1d and Fig.1e). To better illustrate this phenomenon, binary images of high magnifications taken of the microstructure are illustrated in Fig.2. The continuous coarsening of precipitates is clearly traduced by histograms shown in 5. The average size of carbides raises from about 160 nm, before exposure, to about 260 nm after 7OOO hours in furnace. A decrease in coarsening rate can be observed after about 5000 hours (Fig.6). The average grain size, particularly in martensitic steels, cannot be easily revealed. In this case, it may be reasonable to evaluate the size of the lath martensite bloc size, which is a function of the PAGB size. Therefore, for each examined portion, the average bloc size was determined by the intercept technique, curve of bloc size evolution is then plotted (cf. Fig.7). Elemental mapping analysis can reveal the the topologies of precipitates shown in Fig.3.

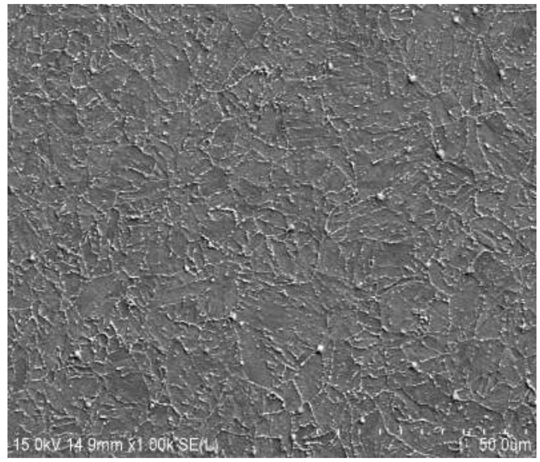
From literature, two topologies of precipitates can be found in 9% Cr ferritic/martensitic steels during exposure; the $M_{23}C_6$ chromium enriched and the Laves phases molybdenum enriched [9; 10]. There is an evidence of chromium enrichment of huge precipitates, after local analysis of several precipitates, we can conclude that the main form of microstructural evolution is the coarsening of secondary carbides. A small amount of Laves phases may be concluded from mapping, the chemical composition can not be carried out because of the small sizes of these phases. But the effect is negligible at temperature of 550°C, that has been proved by previous works [11]. It can be inferred the coarsening and coalescence of precipitates, an enrichment in alloying matrix elements and in particular chromium and molybdenum. Thus, changes in $M_{23}C_6$ lattice parameter after ageing should be studied and could be a significant indicator for assess the effect of the real temperature ageing time of heat-resistant T91 steel. Therefore, the lattice parameter of secondary carbides and matrix obtained can be analysed using the JMA equation:

$$x(t) = 1 - e^{(-kt)^n} \tag{1}$$

Here x(t) represents the changes of $M_{23}C_6$ lattice parameter "a" in time t, k is the lattice transformation rate constant, and n is the Avrami exponent dimensionless constant which is related to the nucleation, growth, or other mechanisms of transformation. Even after long exposure, the average diameter of carbides remain too small to be detected using XRD analysis. Therefore, the electrochemical extraction is necessary to separate the precipitates from the matrix, then the identification will be ensured (Fig.8). The principle of the electrochemical extraction is shown in Fig.9. The obtained filter is then analysed to identify the precipitates present in the bulk material, as well as the associated lattice parameter. For example, in Fig.10. XRD analysis confirm that two topologies of carbides are distinguished: $M_{23}C_6$ carbides and MX carbo-nitrides. At the redaction of these lines, the extractions of the exposed samples are being proceeded. The aim is to determine the lattice parameter of $M_{23}C_6$ carbides, then carry out the temperature time dependence of this parameter and comparing that to close studies. Indeed, Baltusnikas et al. [12] have determined the time-temperature dependence of P91 secondary carbides at temperatures of 600, 650 and 700°C. The obtained equations could be useful as good indicators for the assessment of the temperature time of exposure of 9%Cr heat resistant steels. Authors have predicted, using the obtained curves, the lattice parameter changes in P91 $M_{23}C_6$ carbides. In our work, the objective is to validate this prediction at 550°C through real exposure of samples. More results



(a)



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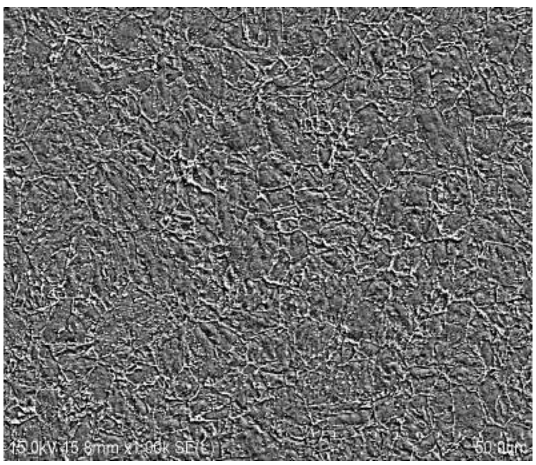

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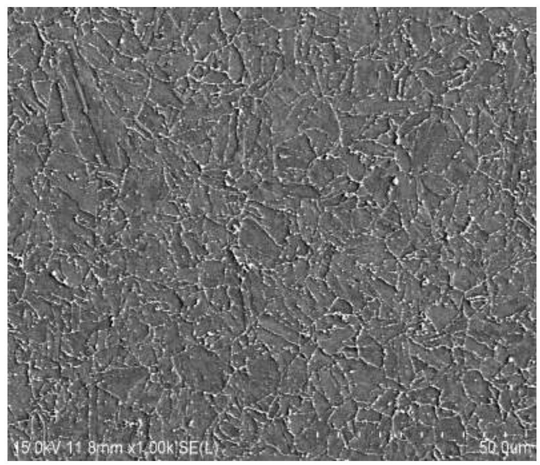

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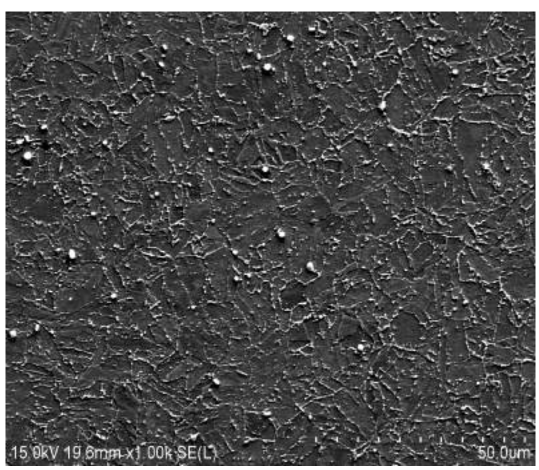

(e)

Figure 1: *SEM micrographs of the modified 9Cr–1Mo steel at 550°C after long durations in furnance: (a) the as-received condition, (b) 1250h, (c) 3000h, (d) 4500h and (e) 7500h*

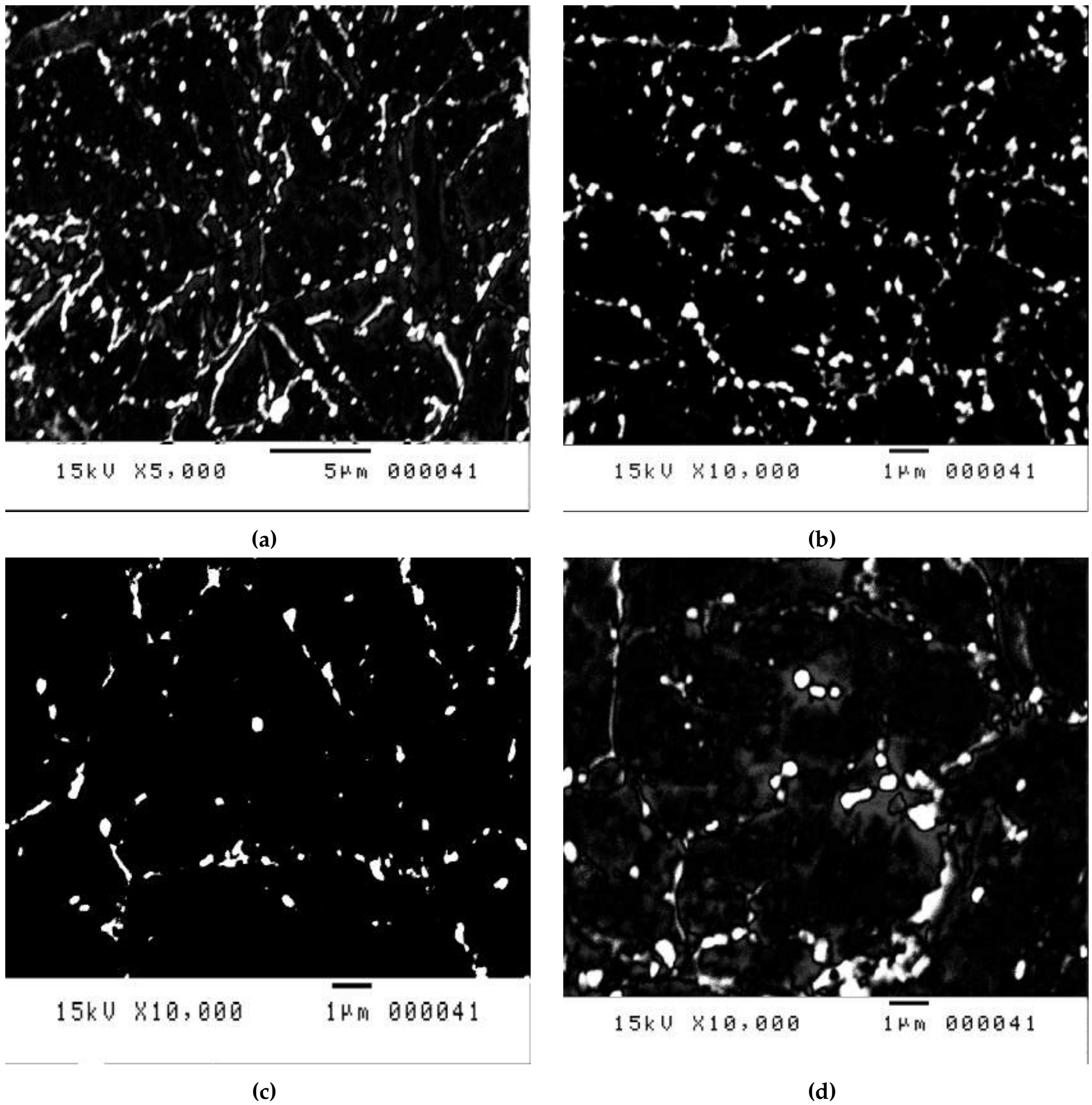

Figure 2: *Binary images of the microstructure of the modified 9Cr–1Mo steel depending on the holding time: (a) the as-received condition, (b) 2160 h, (c) 3000 h and (d) 7000 h*

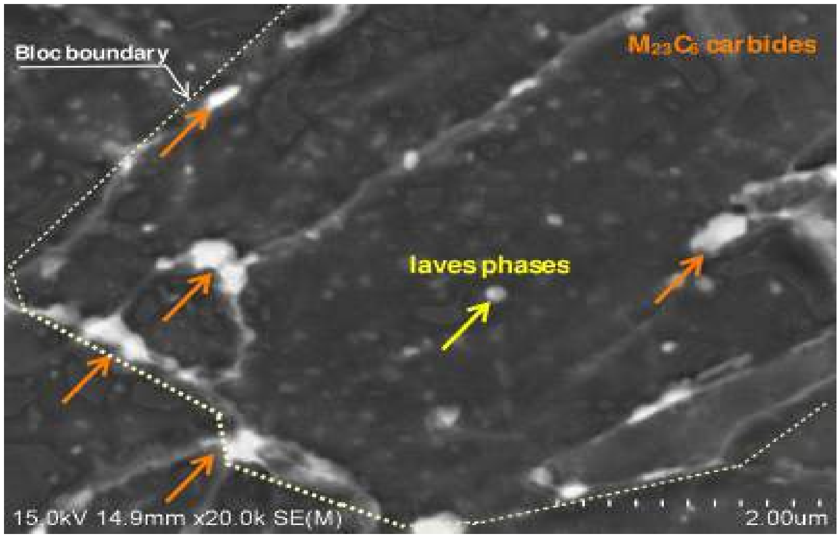

Figure 3: *High magnification micrograph of the studied steel after 7OOO h ageing*

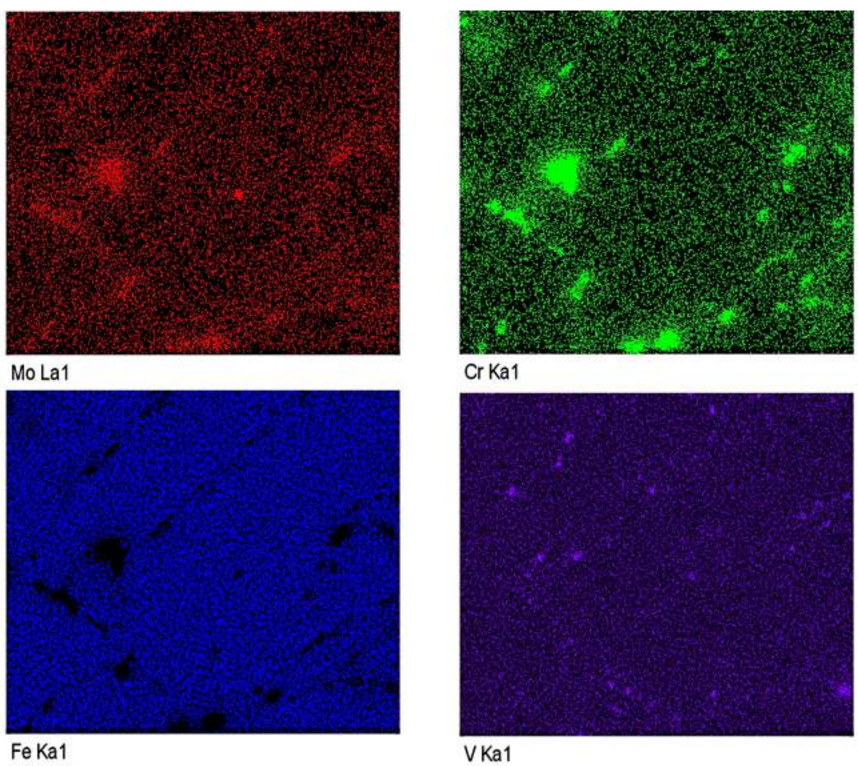

Figure 4: *Elemental mapping analysis basing on Fig.3*

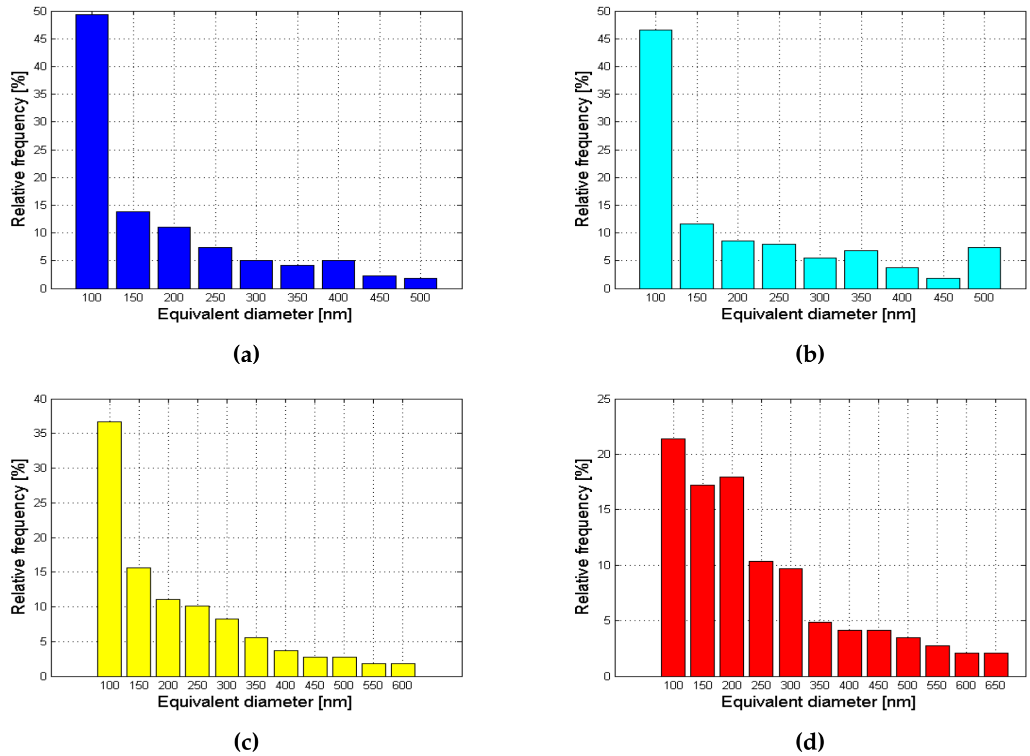

Figure 5: *Size distribution of precipitates after ageing at 550°C for different durations: (a) the as-received condition, (b) 3000h, (c) 4500h and (d) 7000h*

about extraction will be exposed in the conference days.

IV. Conclusions

$M_{23}C_6$ carbide structural and chemical changes during thermal ageing of T91 steel for durations up to 7000 h at 550°C (sub-critical conditions) were investigated. The most important comments about the stability of this steel can be concluded are:

- The tempered lath microstructure is retained even after 7000 h of exposure at high temperatures. Carbides in modified 9Cr–1Mo steel grow with ageing time.

- The coarsening of carbo-nitrides was negligible compared to secondary carbides.

- The effect of Laves phases is negligible.

- The time temperature $M_{23}C_6$ lattice parameter dependence is being analysed with the JMA equation. At the redaction of these lines, the extraction of precipitates is being proceeded and results will be presented.

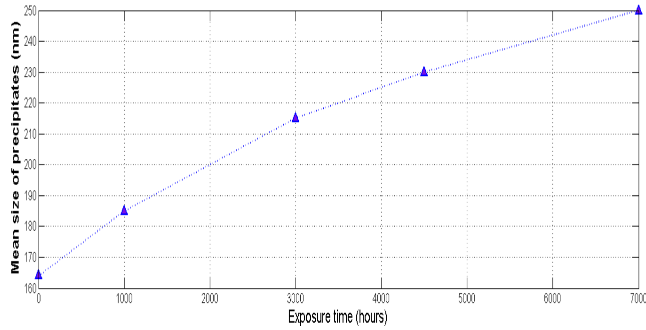

Figure 6: *Growth of precipitates as a function of time ageing in the T91 steel*

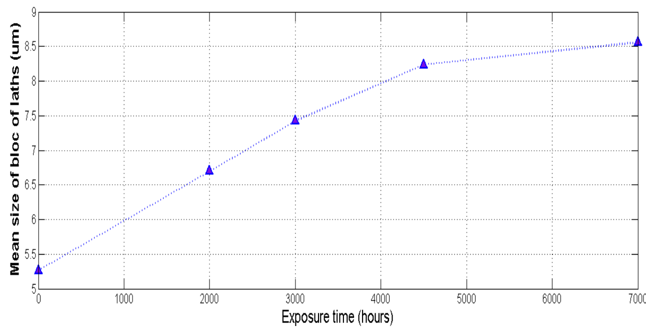

Figure 7: *Growth of bloc boundaries size as a function of time ageing in the T91 steel*

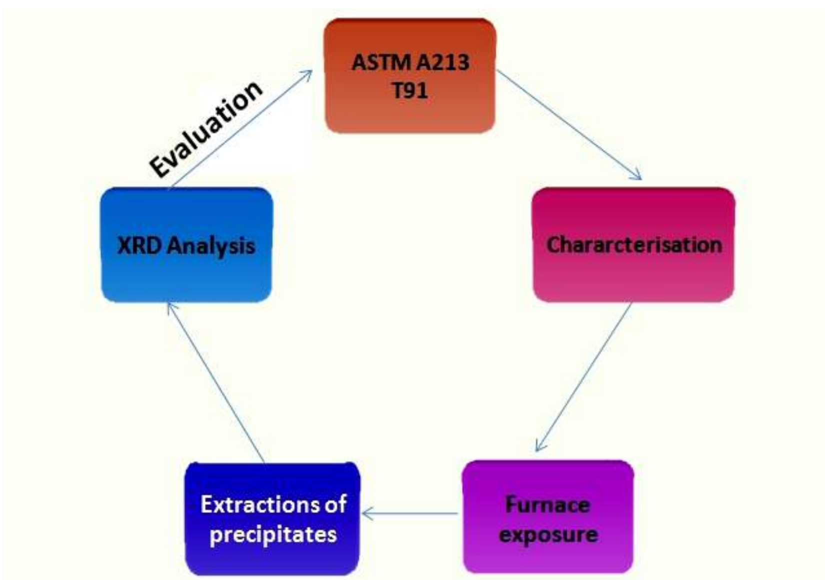

Figure 8: *The emplacement of electrochemical extraction in the evaluation process*

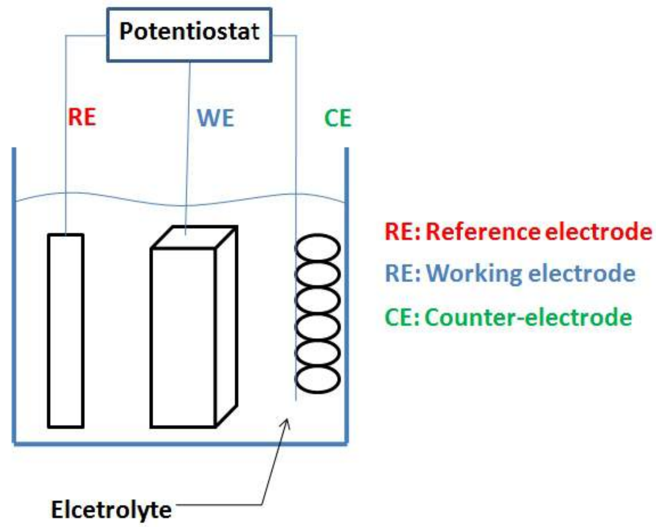

Figure 9: *Schematic illustration of the electrochemical extraction principle*

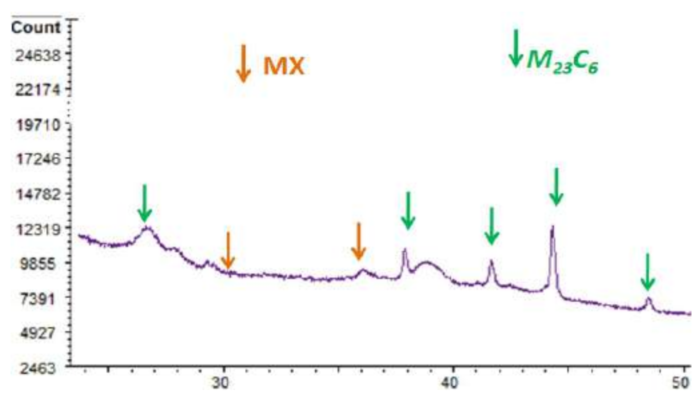

Figure 10: *XRD patterns of residues extracted from T91 steel at the as-received condition*

Acknowledgments

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