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Analysis of Heat Resistant Steel State by Changes of Lattices Parameters of Carbides Phases

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Stability of heat resistant steel crystal structure and carbides lattices parameters during exploitation of power plant is one of the most important factor of reliability and durability of its components. The changes of carbides lattices parameters of pearlite heat resistant 12X1MΦ steel, during long-term operation thermal power plant facilities at 550 °C temperature and 14 MPa pressure and isothermally aged 600 h at 700 °C under laboratory conditions, were analysed. X-ray diffraction method was used for identification of carbides $M_{23}C_6$ and M_7C_3 phases (where M indicates a mixture of metals atoms) and for measurement of accurate lattice parameters of carbides in steel during ageing. At long service times of steel or heating in laboratory conditions, alloying elements Cr, Mo, V replace iron within $M_{23}C_6$ and M_7C_3 carbides, the lattices parameters change and more thermodynamically stable carbides precipitate. The changes of carbides lattice parameters were calculated by structure refinement program Powder Cell and confirmed by GSAS program. Lattice parameter of $M_{23}C_6$ carbide increases with ageing duration of steel and reaches 1.058 nm in steel exploited 227000 h at 550 °C temperature and 14 MPa pressure. The changes of lattice parameters of orthorhombic M_7C_3 are more complicated.

Keywords: heat resistant steel, carbide phase, X-ray diffraction, lattice parameters, Rietveld refinement.

1. INTRODUCTION

Heat resistant steels state assessment the same as reasonable remaining life prediction of high temperature components is of great concern for the high temperature industry both for economic and safety reasons [1]. Many methods and various procedures based on mechanical properties and microstructural deterioration could be performed to gain these objectives. The inspection of creep rupture data and Larson-Miller parameter creep life prediction technique are commonly used to estimate the high-temperature structures [2]. As an alternative way to estimate remaining life predictions, the microstructural characterization methodologies have also been developed, due to the proof of the relationship between the microstructural deterioration and creep rupture life [2].

One of the microstructural criterions – the carbide composition changes in power plant steels as a method of remnant creep life prediction was proposed by R. C. Thomson in the work [3], wherein the chemical composition changes of carbides were related to estimation of the thermal history of power plant steels. There was noted that carbide morphological parameters have significant scattering, even among very similar materials, while compositional parameters changes are much stable. Furthermore, experimental studies using energy-dispersive X-ray analysis of the kinetics of cementite enrichment in steels and simultaneous measurement of particle size and composition over a wide range of tempering times at various temperatures have established the fact that smaller particles enrich more quickly than larger ones [3].

Many of the conventional power plant steels properties depend on heat treatment. After the hardening, normalising and tempering treatment the microstructure of steel usually consists of various fractions of ferrite, bainite and relatively fine particles of cementite whose substitutional solute concentration was initially similar to the solute content of the steel as a whole. This is known to produce good creep properties in the short term. These carbides were far from their equilibrium chemical composition, size and shape. During long-lasting exploitation of steel the metastable bainitic microstructure decomposes when service high temperature and creep have influenced. The cementite tends to approach its equilibrium composition in regard to the substitutional elements. Eventually the dissolution of cementite starts and more thermodynamically stable secondary alloy carbides precipitation, rich in Mo and Cr, and wasted in Fe, then result. This process is especially important for low alloy steels in which the enrichment kinetics of alloy carbides at the expense of cementite are fairly slow and the considerable amount of cementite fraction can remain during useful service life of steel. This fact can be applied as a quantitative estimation of the thermal history of the component [3].

On the other hand, many of researchers have used the secondary carbide precipitation sequence in steels as a criterion of service life assessment [4, 5].

Power plant components of low alloy steel 12X1MΦ (Russian grade) have good high temperature creep properties and scaling resistance, and are widely used in the construction of Lithuanian industrial plant operating at 550 °C temperature and 14 MPa pressure.

Previously, the carbide precipitation sequence in steel 12X1MΦ exploited different time has been examined for purpose of estimation the thermal history of steel [6].

It has been suggested by a number of authors that measurements at temperatures higher than those used in normal service to accelerate the evolution of microstructure may not accurately predict the microstructures found in exploited steel [4]. Other researchers have offered an

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opinion that such measurements produce more characteristic parameters of the true thermal history of the component especially if correct scientific method is applied [7].

Recently, the carbide precipitation sequence of steel 12X1MΦ isothermally aged in laboratory conditions at 600, 650 and 700 °C have been reported [8]. It was proved that the evolutionary sequence of carbides in steel aged at elevated temperatures is the same as in the exploited steel. In the light of these results the Bragg peaks integrated intensity changes of carbide phases have been proposed for thermal history assessment of ex-service steel [8]. However this methodology is limiting to a quite short service time of steel due to the termination of changes of integrated intensities which achieve a constant value after not long service duration. The precision of integrated intensities quantitatively measurements again are quite complicated since the prepared samples must not be affected by a presence of preferred orientation and measurements conditions must be held unchangeable.

Therefore, the purpose of this work is to determine the structural parameter suitable as a criterion for thermal history estimation of power plant steel 12X1MΦ, which would be suitable over all service life of steel. In our view such a criterion could be the crystal lattice parameter of carbide phase. The lattice parameter can be simply determined from any carbide residue by XRD. Our thought originated from the previous declare that in the virgin steel state of the cubic carbide $M_{23}C_6$, which crystal lattice parameter $a = 1.064$ nm decreases to the 1.052 nm due to the diffusion of molybdenum atoms when the service time of steel reaches the last stage. Molybdenum atoms in carbide $M_{23}C_6$ change chromium and compound becomes $Fe_{21}Mo_2C_6$ [6]. But this conclusion is rather strange because the Mo atom is bigger then Cr, so the crystal lattice parameter of $M_{23}C_6$ have to increase. Exactly in this work we have shown the carbide $M_{23}C_6$ cubic lattice parameter a increases with ageing and exploiting time of steel.

2. EXPERIMENTAL

X-ray diffraction (XRD) measurements were carried out with CuK_α radiation ($\lambda = 0.15405$ nm) on a DRON diffractometer operating at 35 kV and 20 mA equipped with a single-crystal graphite monochromator in step scanning mode of 0.02º in 2θ and counting time of 0.5 s per step. The XRD patterns were collected with internal standard silicon to have good precision of the lattice parameter values. The recording of XRD patterns were repeated 10 times for each specimen and averaged to obtain accurate counting statistics. The data were fitted with the Powder Cell [9] and GSAS+EXPGUI [10, 11] programs based on the Le Bail pattern-decomposition [12] and Rietveld refinement [13, 14] methods.

In the present XRD study, the accurate lattice parameters of carbides $M_{23}C_6$ and M_7C_3 of steel 12X1MΦ have been measured. The samples examined here were cut from heat resistant steel 12X1MΦ taken from "Lietuvos Elektrinė" power station. The virgin samples were aged in laboratory conditions at 700 °C for various times. Other samples were prepared from steels exploited for 151000 h and 227000 h. Typical operating conditions for this steel are 550 °C and at pressures of 14 MPa.

Carbide phase of steel was highlighted during the electrochemical etching of the steel samples (measurements (20×10×10) mm) in 5 % hydrochloric acid solution thus relatively increasing carbide concentration on the samples surface. Power supply 1621A BK Precision was used for this process. Electrochemical etching at (130 – 150) mA/cm^2 current densities lasted for 1 hour. Then samples were taken from the electrolyte solution, washed by warm water weak flush and dried in a hot air stream. Surface of every sample was covered by small amount of silicon standard powder.

The XRD data on transformation kinetic of heat resistant steel carbides lattice parameters were analyzed using a classical John-Mehl-Avrami (JMA) equation for isothermal conditions [15, 16]:

$$x(t) = 1 - \exp\left[-(kt)^n\right], \quad (1)$$

where $x(t)$ is the change of lattice parameter a at time t, k is the lattice transformation rate constant, t is time, and n is a constant, which can be related to different materials phases growth, nucleation, crystallization.

John-Mehl-Avrami equation can be linearized in form [17]:

$$\ln\left[-\ln\left(1 - x(t)\right)\right] = n \ln k + n \ln t\ . \quad (2)$$

In addition, this equation can be applied to a wide range of other problems, from the crystallization kinetics of different materials, analysis of depositions in surface science, to ecological systems. However most of the applications of the JMA equation have been the study of phase transformations in three dimensional systems.

3. RESULTS AND DISCUSSION

The example of XRD patterns of highlighted carbide residues from different time exploited and laboratory aged 12X1MΦ steel are presented in Figure 1.

Only three XRD curves are shown for purpose of clarity. The shifts of Bragg peaks (420) and (422) (diffraction angles respectively $2\theta \sim 38º$ and $2\theta \sim 42º$) for carbide $M_{23}C_6$ are very clearly distinguishable. The same results with carbide M_7C_3 which Bragg peaks (150) and (112) (diffraction angles $2\theta \sim 39.5º$ and $2\theta \sim 42.8º$, respectively) are shifted too visibly.

The problem of overlapping Bragg peaks of several carbides was solved by application whole powder pattern fitting programs Powder Cell and GSAS+EXPGUI, by which accurate crystal lattice parameters were determined. Powder Cell program was used due to having a very easy interface for performing simple Le Bail fitting to the raw diffraction data. Although refinement was not fully satisfying (Fig. 2) but the obtained results (profile agreement factor $Rp = 0.14$ and weighted profile agreement factor $Rwp = 0.21$) looks like promising.

The analysis of each powder pattern data sets was carried out using the started models consisted of the room temperature structures: silicon (cubic, Fd3m) [18], vanadium carbide (cubic, Fm-3m) VC [18], carbide (cubic, Fm-3m) $M_{23}C_6$ [19, 20] and carbide (orthorhombic, Pnma) M_7C_3 [20].

The $M_{23}C_6$ carbide crystallizes in a cubic face-centered lattice in the space group Fm-3m with 92 metal atoms

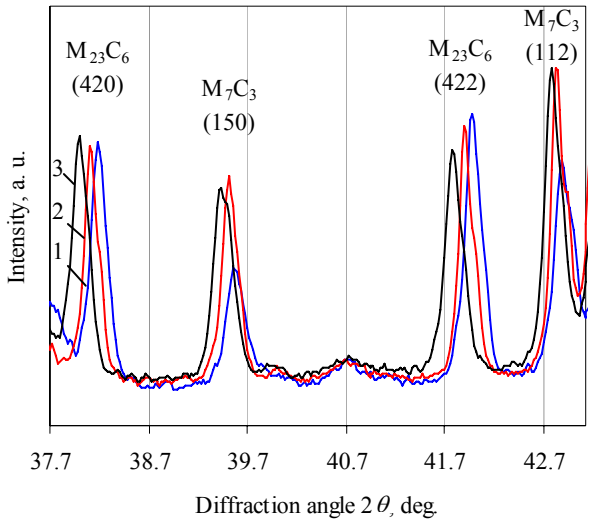

Fig. 1. X-ray diffraction patterns of steel 12X1MΦ, curves: 1 – aged for 42 h at 700 ºC, 2 – aged for 288 h at 700 ºC and 3 – exploited for 227000 h at 550 ºC temperature and 14 MPa pressure

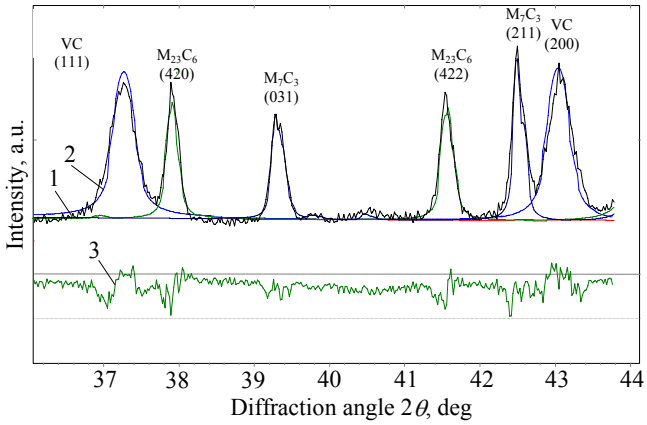

Fig. 2. The observed and calculated powder diffraction patterns of carbide phases residues of steel (exploited for 227000 h at 550 ºC temperature and 14 MPa pressure) after the final Le Bail fitting refinement by Powder Cell program. Curves: 1 – observed, 2 – calculated and 3 – difference

located at the 4(a), 8(c), 32(f), and 48(h) symmetry sites. At these sites different metal atoms could exchange each other due to diffusion when steel is exposured to the high temperature and pressure. The geometrically close-packed 4(a) sites are substituted with iron atoms. The sites 48(h) and 32(f), bonded to carbon atoms, are less favourable for iron substitution. In long lasting temperature effect the large molybdenum atoms tend to occupy exclusively 16-coordinated 8(c) sites. Carbon atoms are most probably placed on 24(e) sites [18].

The fitting of the XRD data by the Powder Cell was started from the refinement of the first structural parameter – zero-shift of powder pattern and the precise lattice parameter $a = 0.543088$ nm of silicon was held not refined. Simultaneously scale factors and peaks breadth were refined.

Then remaining carbide structures were refined holding fixed zero-shift, which was obtained at first stage. At the same time scale factors, peaks breadths and accurate crystal lattice parameters of every carbide phases were refined.

The crystal lattice parameters determination of carbide $M_{23}C_6$ again were checked by GSAS+EXPGUI program, which are complicated but more rigorous Rietveld refinement programs then Powder Cell, and could give better fitting. The example of crystal lattice parameter refinement by GSAS program is presented in Figure 3.

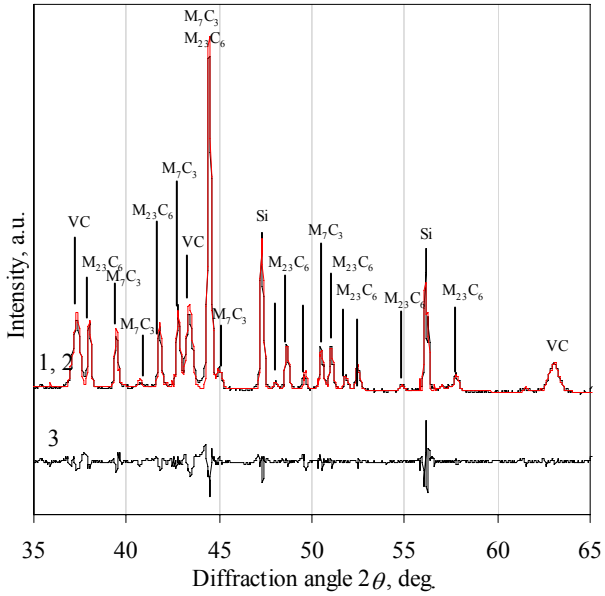

Fig. 3. The observed and calculated powder diffraction patterns of carbide phases residues of steel (exploited for 227000 h at 550 °C temperature and 14 MPa pressure) after the Rietveld refinement by GSAS program. Curves: 1 – observed, 2 – calculated and 3 – difference

The difference between the observed and computed data (lower black line) and fitted agreement factors ($Rwp = 0.14$, $Rp = 0.096$) shows better results of refinement than with Powder Cell. Some deviation of difference curve is due to complexity of refining procedure, so not all structure parameters were fitted. The calculated lattice parameter $a = 1.05778$ nm by GSAS program is very similar to parameter $a = 1.05775$ nm calculated by Powder Cell, so such complex program like GSAS isn't rational to apply for simple calculations.

Similarly, the lattice parameters a, b and c of orthorhombic carbide M_7C_3 for virgin, aged in laboratory conditions and exploited steel samples were determined by program Powder Cell. The obtained changes of lattice parameters show more complicated dependences versus ageing or exploiting time then for cubic carbide $M_{23}C_6$. At first stage of steel ageing at 700 °C the parameters a and e decreases, then they started to increase while parameter c at first increases and later obtained constant value $c = 1.20238$ nm, which doesn't change even after 227000 h service time. For this reason the further investigations at lower temperatures is necessary to obtain transformation kinetics of the carbide lattice parameters.

The refined data ($M_{23}C_6$ lattice parameters changes) are plotted in Figures 4 and 5. The graphs of $\ln\ln[a_{max}/(a_{max}-a_t)]$ v.s. $\ln t$ are linear, the implication is

that the transformation conforms to the Johnson-Mehl-Avrami equation.

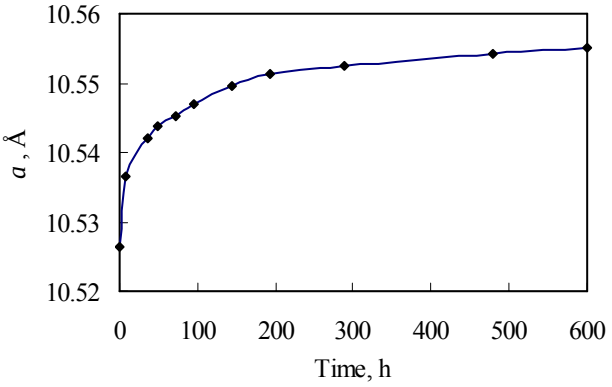

Fig. 4. Transformation of lattice parameter a of $M_{23}C_6$ carbide as a function of time during ageing of steel at 700 °C temperature

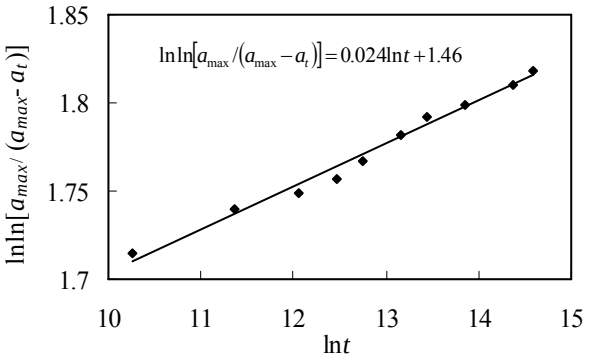

Fig. 5. Transformation kinetic follows the Johnson-Mehl-Avrami equation for $M_{23}C_6$ in 12X1MΦ steel during its ageing at 700 °C temperature

Authors according equation of Fig. 5 have calculated transformation rate constant $k = 1.06 \cdot 10^{-26}$ of $M_{23}C_6$ carbide lattice parameter. Activation energy of the lattice parameters transformation during steel aging will be obtained in the future analysis after experiments at two additional temperatures.

The lattice parameter of carbide $M_{23}C_6$ was determined for virgin, aged in laboratory condition for 600 h at 700 °C temperature and exploited 151000 h and 227000 h at 550 °C temperature and 14 MPa pressure steel samples. The carbide $M_{23}C_6$ cubic lattice parameter a increases from initial 1.05265 nm value to 1.05551 nm with ageing time of samples in laboratory conditions but doesn't reache a value (1.05621 nm for 151000 h and 1.05775 nm for 227000 h) of exploited steel. Many researchers have suggested that the transformation of lattice of $M_{23}C_6$ type carbides during steel ageing would involve the diffusion of carbon and alloying elements [3, 21].

The diffusion coefficient D in steel can be expressed as below [22]:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (3)$$

where D_0 is the pre-exponential term in diffusion coefficient, Q is the activation energy, R is the universal gas constant.

It was established that diffusion coefficient of molybdenum at 560 °C is $4.75 \cdot 10^{-21}$ m^2s^{-1} [21], chromium – $1.37 \cdot 10^{-19}$ m^2s^{-1} and carbon is $1.5 \cdot 10^{-11}$ m^2s^{-1} respectively and shows a high sensitivity to temperature (e. g. D of molybdenum at 700 °C reaches $4.78 \cdot 10^{-18}$ m^2s^{-1}) [3].

In the present investigation, alloy carbide transformation involves the diffusion of chromium, molybdenum and carbon, the diffusivities of which are different at the transformation temperature. The main factor affecting the transformation rate of carbide lattice parameters is diffusion coefficient of alloying elements. The change of lattice parameter is related also with the size of molybdenum atoms that are 10 % larger than chromium. Parameters and composition of carbide lattice depends on steel ageing temperature due to the diffusion coefficients dependence on temperature according Ahhrenius eq. (3). After ageing at exploitation temperature, the quantity of molybdenum atoms in the alloy carbides had increased. This transformation occurs mostly at lower temperatures and needs long enough time. It is submitted that the variations illustrate local differences in ease of diffusion of Mo to the $M_{23}C_6$, the process that effects the replacement of Cr by Mo to form the more stable carbide structure. Ageing of steel in laboratory conditions at 700 °C temperature for 600 h isn't enough term for replacement of all chromium atoms in $M_{23}C_6$ carbide by molybdenum due to its lower diffusion coefficient than chromium.

4. CONCLUSIONS

The methods of Rietveld or Le Bail (like GSAS, Powder Cell or others) refinement are highly suitable for complex structures parameters determining.

The lattice parameter a of cubic carbide $M_{23}C_6$ of 12X1MΦ steel isothermally aged at 700 °C temperature for 600 h increases from 1.05265 nm to 1.05551 nm due to the diffusion of alloying elements (chromium and molybdenum) atoms.

The lattice parameter a of carbide $M_{23}C_6$ residue from exploited for 227000 h steel 12X1MΦ have reached a = 1.05775 nm due to the diffusion of molybdenum atoms when the service time of steel reaches the last stage.

The transformation rate of lattice parameters depends on the ageing or exploitation temperature of steel. The refined data – $M_{23}C_6$ lattice parameters changes – conforms to the Johnson-Mehl-Avrami equation and according to this equation transformation rate constant $k = 1.06 \cdot 10^{-26}$ was calculated.

The lattice parameter of carbide $M_{23}C_6$ of 12X1MΦ steel continuously increases with exploiting time. This result is very important and could be applied for 12X1MΦ steel state assessment and remnant life prediction.

Changes of lattice parameters a, b and c of orthorhombic carbide M_7C_3 of steel 12X1MΦ aged in laboratory conditions and exploited are complicated and require further investigations.

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