

Investigations of carbide precipitates in modified 9 % Cr steel using different electron spectroscopy techniques

Preiskava karbidnih izločkov v modificiranem jeklu z 9 % Cr z uporabo različnih elektronskih spektroskopskih metod

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Abstract: For characterization of carbide precipitates in modified 9 % Cr steel we used a multitechnique approach based on electron beam, combining field emission scanning electron microscopy (FE-SEM), Auger electron microscopy (AES) and energy dispersive X-ray spectroscopy (EDXS). In this paper the principles of the analytical methods are explained and their complementarity is demonstrated.

Izveček: Za preiskavo karbidnih izločkov v modificiranem jeklu z 9 % Cr smo uporabili različne metode na osnovi elektronskega curka. Kombinirali smo vrstično elektronsko mikroskopijo na poljsko emisijo (FE-SEM), Augerjevo elektronsko mikroskopijo (AES) ter energijskodisperzijsko spektroskopijo rentgenskih žarkov (EDXS). V tem prispevku smo skušali prikazati osnove analitičnih metod in njihovo komplementarnost.

Key words: FE-SEM, AES, EDXS, steel, carbide precipitates

Ključne besede: FE-SEM, AES, EDXS, jeklo, karbidni izločki

INTRODUCTION

Electron spectroscopy techniques are techniques that use the interaction of high energy electrons with a sample to perform an analysis. For the characterization of the microstructure we used a multi-technique approach based on electron beam, combining field emission scanning electron microscopy (FE SEM), Auger electron microscopy (AES) and energy dispersive x-ray spectroscopy (EDXS). Auger electron spectroscopy (AES) and energy dispersive x-ray spectroscopy (EDXS) are both analytical techniques used for the elemental analysis or chemical characterization of samples. However, AES is a surface sensitive technique, while EDXS is not. The aim of the present work was to demonstrate the carbide precipitates investigation in vanadium and niobium modified creep-resistant 9 % Cr steel by using FE SEM, AES and EDXS, and especially, to explain the principles, specialities as well as the advantages and disadvantages of particular technique.

The microstructure of modified 9 % Cr steel consisted of tempered martensite containing $M_{23}C_6$ carbide particles formed during a final normalizing and tempering heat treatment. The thermal stability of $M_{23}C_6$ is relatively high, which produce the basic creep strength by precipitating on subgrain boundaries during tempering. The $M_{23}C_6$ carbides

increase creep strain in these alloys by retarding subgrain growth, which is a major source of creep strain. In modified 9 % Cr steel there are also MX precipitates present i.e. VN and Nb(C, N). During the creep exposure, the precipitation of Laves phase and additional precipitation of VN and Nb(C, N) take place. The introduction of MX precipitates in modified 9 % Cr steel by alloying with V, Nb and N can improve creep rupture strength by approximately 50 % at 600 °C. A fine distribution and high thermal stability of the carbide and nitride particle is a key to high creep strength. It is well known that microstructural evolution of steels determines the life and long time behavior of the material To evaluate service time of the components it is very important to characterize the microstructure.^[1-6]

THEORETICAL BACKGROUND

Electron bombardment of a sample produces a large number of effects in a sample because the incident electrons interact with specimen atoms in a variety of ways (Figure 1). These effects allow us to use different electron spectroscopy techniques in analysing sample.

In the present work we have been focused only on the secondary electrons used for imaging and characteristic x-rays and Auger electrons used for the analysis.

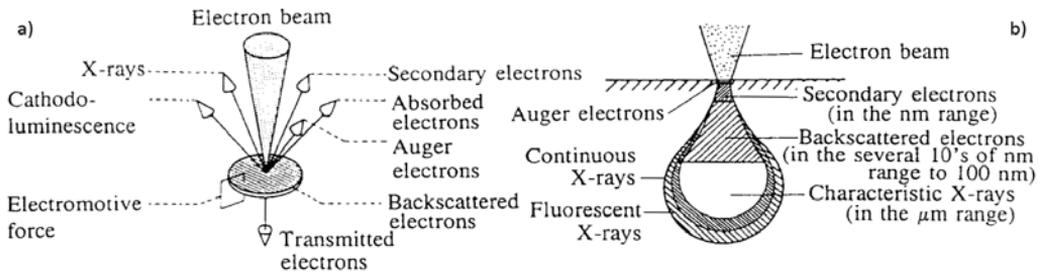


Figure 1. The effects produced by electron bombardment of the material: a) shows the different type of information obtained; b) shows the regions from which the information is generated.

Secondary electron imaging (SEI)

The incident electrons cause electrons to be emitted from the sample due to elastic and inelastic scattering events within the sample's surface and near-surface material. Emitted lower-energy electrons resulting from inelastic scattering are called secondary electrons.

To create an image, the incident electron beam is scanned in a raster pattern across the sample's surface. The emitted secondary electrons are detected for each position in the scanned area by an electron detector. The topography of surface features influences the number of electrons that reach the secondary electron detector from any point on the scanned surface. This local variation in electron intensity creates the image contrast that reveals the surface morphology. Therefore, secondary electrons provide high-resolution imaging of fine surface morphology.

Auger electron spectroscopy (AES)

AES is one of the most commonly used

techniques for surface analysis and it is used to determine the atoms present at a surface, their concentrations and also their chemistry. Auger electrons with a characteristic kinetic energy can only escape from the outer 0.5–5 nm of a solid surface. This effect makes AES an extremely surface sensitive technique. Auger electron emission (Fig. 2) is one of the two possible relaxation mechanisms for an excited atom with a vacancy in a core level.

The ground state of the system is shown in Figure 2a). In Figure 2b) an incident electron has created a hole in the core level K by ionization. The hole in the K shell is filled by an electron from L_2 , releasing an amount of energy ($E_K - E_{L_2}$) which can be given to another electron. In this example the other electron is in the L_3 shell, and it is then ejected with energy ($E_K - E_{L_2} - E_{L_3}^*$). $E_{L_3}^*$ is the binding energy not of L_3 in its ground state, but in the presence of a hole in L_2 . The doubly ionised final state is shown in Figure 2c).

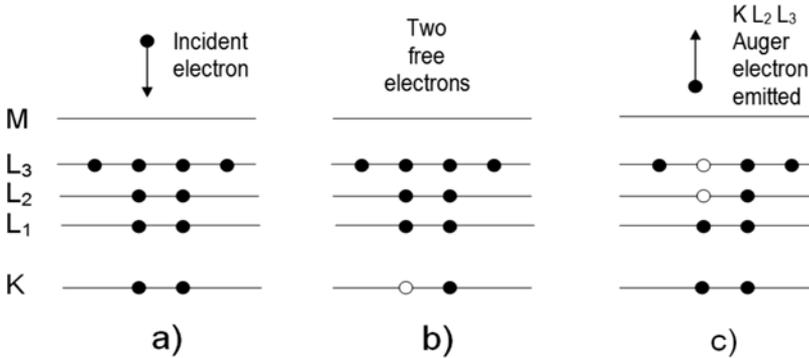


Figure 2. Schematic diagram of the process of Auger emission in a solid.

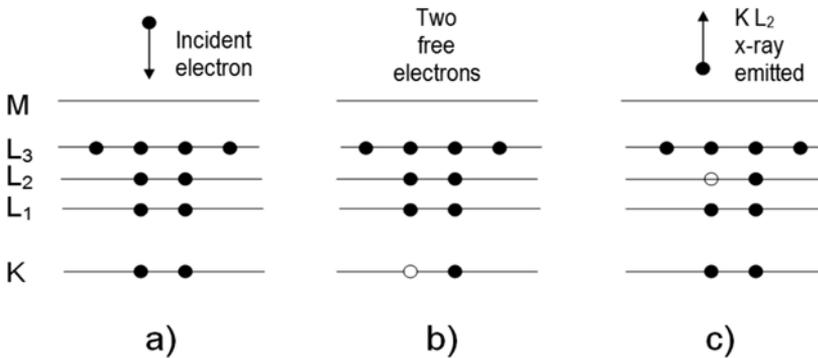


Figure 3. Schematic diagram of X-ray emission.

Energy dispersive X-ray spectroscopy (EDXS)

The other relaxation mechanism is x-ray fluorescence, in which an x-ray is emitted instead of an Auger electron (Figure 3). The x-ray emission is generated by beam of energetic electrons when it impinges on a specimen. As it has already been explained in the process of Auger electron emission an incident electron (Figure 3a) has created a hole in the core level K by ionization (Figure 3b). The hole in the K shell is then filled by an electron from

the L_2 , releasing an amount of energy ($E_K - E_{L_2}$). Instead of giving the energy to another electron as in the case of Auger electron emission (Figure 2c), this energy can appear as an x-ray of energy $h\nu = (E_K - E_{L_2})$ (Figure 3c). With heavier elements, x-ray emission is more likely, while with lighter elements, the probability of Auger emission increases and x-ray emission decreases.

Energy dispersive x-ray spectroscopy (EDXS) is thus, an investigative meth-

od which exploits x-ray emission and is commonly used in an SEM for the elemental identification and quantification of sample chemical composition. The x-rays depending on accelerating voltage and material density are generated in a region about 1–3 μm in depth, and therefore EDXS is not a surface science technique.

EXPERIMENTAL PROCEDURE

The investigated material is a section of steam pipe made of modified 9 % Cr steel which has been in service for 10 000 h at about 550 °C. Samples were metallographically prepared for microstructural characterization by grinding, polishing and etching in a water solution of ferric chloride with addition of HCl (5 %). AES investigations were carried out in a Micro-lab 310F VG-Scientific instrument. A primary electron beam of 10 keV was used. FE AES studies were performed after removing amorphous C and O by Ar^+ ion sputtering. EDXS analyses were carried out on a FE-SEM (Jeol JSM-6500F) equipped with INCA Energy 400 ED spectrometer. EDXS analyses were performed at several spots using two different accelerating voltages, namely 10 kV and 20 kV. After EDXS points analyses also EDXS maps were done using accelerating voltage of 10 kV to show the elemental distribution.

RESULTS AND DISCUSSION

Auger electron spectroscopy (AES)

As it has already been mentioned, the AES analysis was performed in several spots (Figure 4) after removing adsorbed amorphous C and O by Ar^+ ion sputtering.

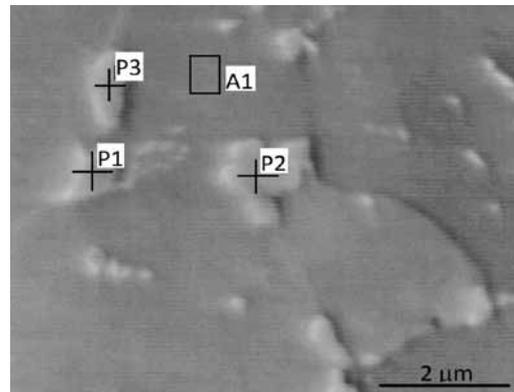


Figure 4. SE image of the microstructure of modified 9 % Cr steel where AES analyses were performed.

The AES analyses of the precipitates (P1, P2 and P3 in Figure 5) reveal the presence of Fe, Cr, Mo and C (Figure 5). However, AES analysis of the matrix (A1 in Figure 5) shows no Auger peaks from Mo or Cr because their concentration in the matrix is below the detection limit for the AES. The oxygen Auger peaks can be seen on AES spectra are due to contamination because of a longer duration of the analysis. Despite UHV conditions inside the vacuum chamber of the SEM/AES apparatus there are

still present molecules of oxygen which adsorbed on the surface after sputtering.

An enlarged detail of carbon peak obtained by AES analysis of the precipitates (Figure 6) shows a typical carbidic shape. That means that the investigated precipitates are carbides.

AES point analyses made on the carbide precipitate and matrix (Figure 7) indicate that the carbides are not homogenous but are mixed iron-chromium-molybdenum carbides (Figure 8). The oxygen peak is, again, because of contamination of the surface of specimen in the vacuum chamber because of longer duration of the analyses.

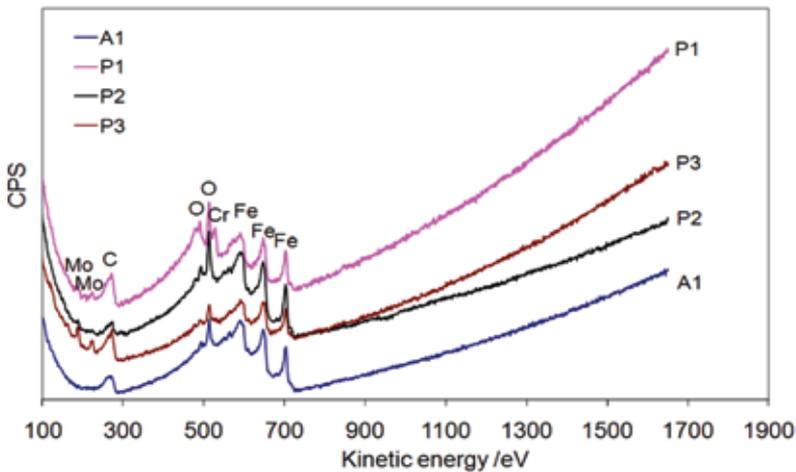


Figure 5. Auger spectra in P1, P2, P3 and A1

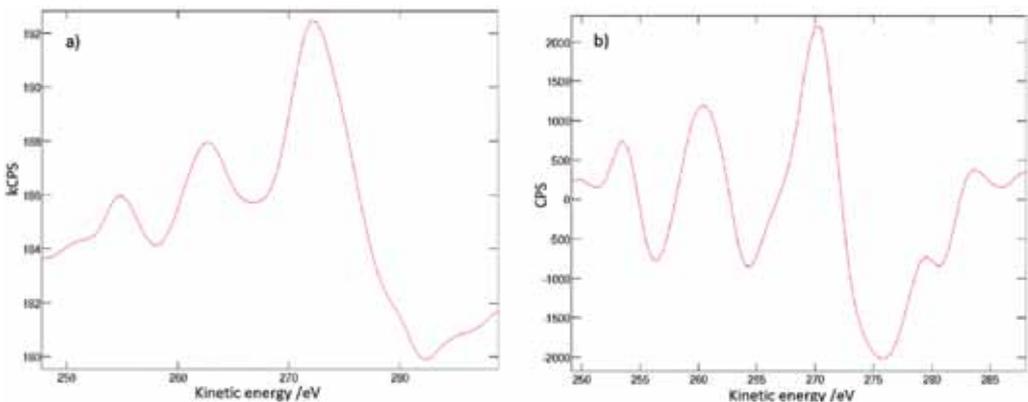


Figure 6. Auger spectra from carbide: a) direct spectra; b) derivative spectra

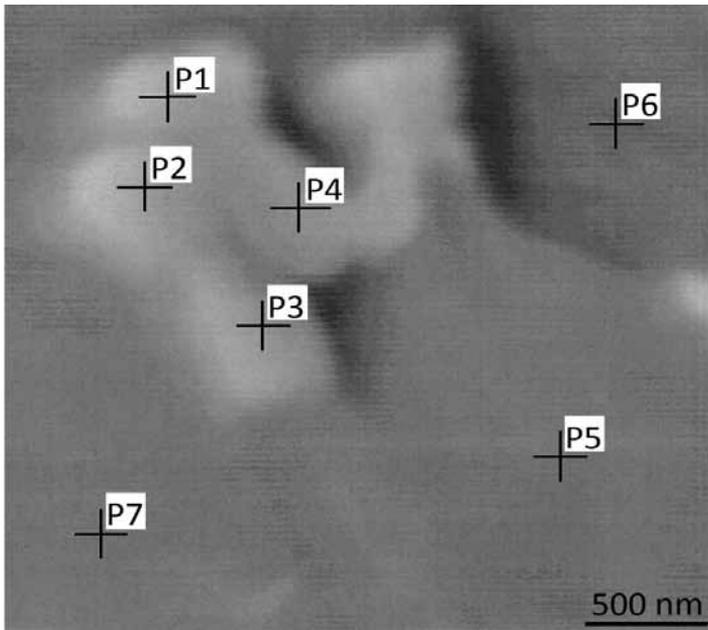


Figure 7. SE image of the area where AES point analyses were performed

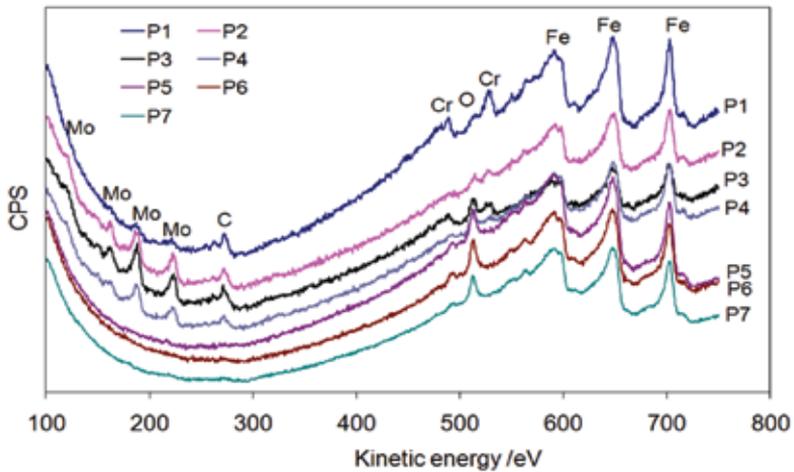


Figure 8. Auger spectra in P1, P2, P3, P4, P5, P6 and P7

Energy dispersive X-ray spectroscopy (EDXS)

The EDXS analyses of carbide precipitates (Figure 9) were performed at different accelerating voltages of incident electron beam, namely 10 kV and 20 kV, respectively.

The results of EDXS analyses performed with the accelerating voltage of 20 kV show smaller concentrations of Cr, Mo, C and Si in precipitates than at 10 kV (Table 1). The reason for this lies in different size of analysed volume. The smaller the accel-

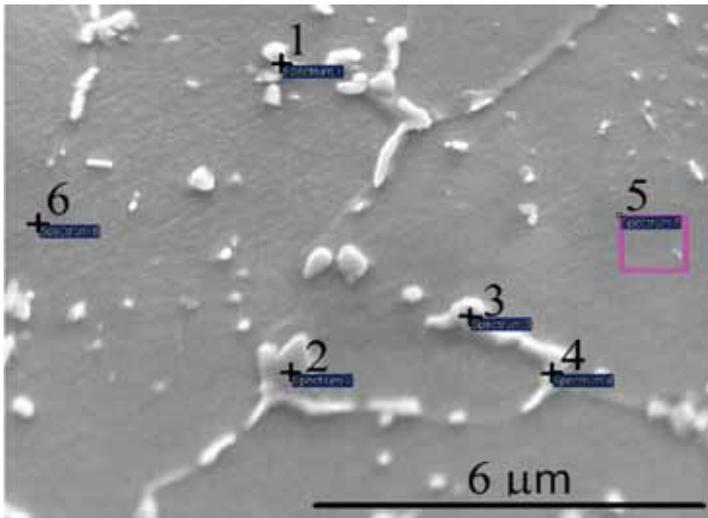


Figure 9. SE image of microstructure of modified 9 % Cr steel where EDXS analysis was made

Table 1. Material composition of different elements at several spots using different accelerating voltages of incident electron beam.

AC = 20 kV	Concentration in mole fractions, x/%					
	C	Si	Cr	Fe	Ni	Mo
Spectrum 1	19.51	0.63	11.22	65.94	1.16	1.53
Spectrum 2	13.43	1.36	7.11	72.88	3.00	2.22
Spectrum 3	13.57	1.39	6.52	73.19	2.85	2.49
Spectrum 4	16.45	1.86	7.67	66.84	3.16	4.02
Spectrum 5	7.57	0.40	3.56	86.14	1.99	0.35
Spectrum 6	7.29	0.42	4.81	85.74	1.74	0.00
AC = 10 kV	Concentration in mole fractions, x/%					
	C	Si	Cr	Fe	Ni	Mo
Spectrum 1	20.88	0.48	22.17	53.19	0.56	2.71
Spectrum 2	14.10	1.59	6.04	72.85	1.45	3.97
Spectrum 3	14.64	1.76	10.11	67.15	2.03	4.31
Spectrum 4	22.47	3.02	14.56	48.92	2.20	8.83
Spectrum 5	7.72	0.19	4.42	86.50	0.80	0.36
Spectrum 6	5.68	0.15	2.36	90.28	1.52	0.00

erating voltage is the smaller is analysed volume. Thus, the characteristic x-rays at accelerating voltage of incident electron beam of 20 kV come not only from the carbide precipitates but also from a larger region of surrounding matrix, which consists of lower concentrations of Mo, Cr and C than precipitates.

Although the analysed volume is smaller in the case of using 10 kV, some part of x-rays during EDXS analysis of precipitates still comes from the matrix. Therefore, Ni and Si were obtained by the analyses of the carbides and the content of Fe is higher than it should be. The EDXS analysis of carbon is problematic as well. Since the applied scanning electron microscope is not equipped with cold trap that would absorb the residual gases, the carbon present in vacuum chamber is baked on the specimen surface by electron beam. Thus, a content of C, especially in the matrix is too high.

Since better EDXS quantitative results were obtained at lower accelerating voltage of incident electron beam also EDXS maps were recorded at 10 kV (Figure 10). EDXS maps which show the elemental distributions confirm that the precipitates are richer in C, Mo and Cr than the matrix. As well as EDXS point analyses also EDXS map of Si shows an

increased concentration of Si in the carbide precipitates according to the matrix. It has been suggested that this is not due to the presence of Si in the precipitates but because of the enrichment of Si close to $M_{23}C_6$ /matrix interface, since the solubility of Si in these carbides is very low.^[4]

Because AES is a surface sensitive technique and EDXS is not, the spatial resolution of AES and EDXS differ significantly. The advantage of AES is the information about the chemical state of the present element which can be obtained from AES spectrum. AES of the precipitates showed that carbon line shape was typical for carbide and thus, it can be concluded that carbon in the precipitates was present as carbide. However, the quantitative AES analysis is not as precise as in the case of EDXS analysis and, thus, it was not even performed. The first reason lies in the sensitivity factors for AES quantitative analysis which are not well determined for compounds, while the second is signal-to-noise ratio which is much better in the case of EDXS.^[7] However, none of these two techniques are the most proper for the determination of type of the carbides. For that purpose diffraction techniques, for instance transmission electron microscope (TEM), X-ray diffraction (XRD) or electron backscatter (EBSD) are much better choice.

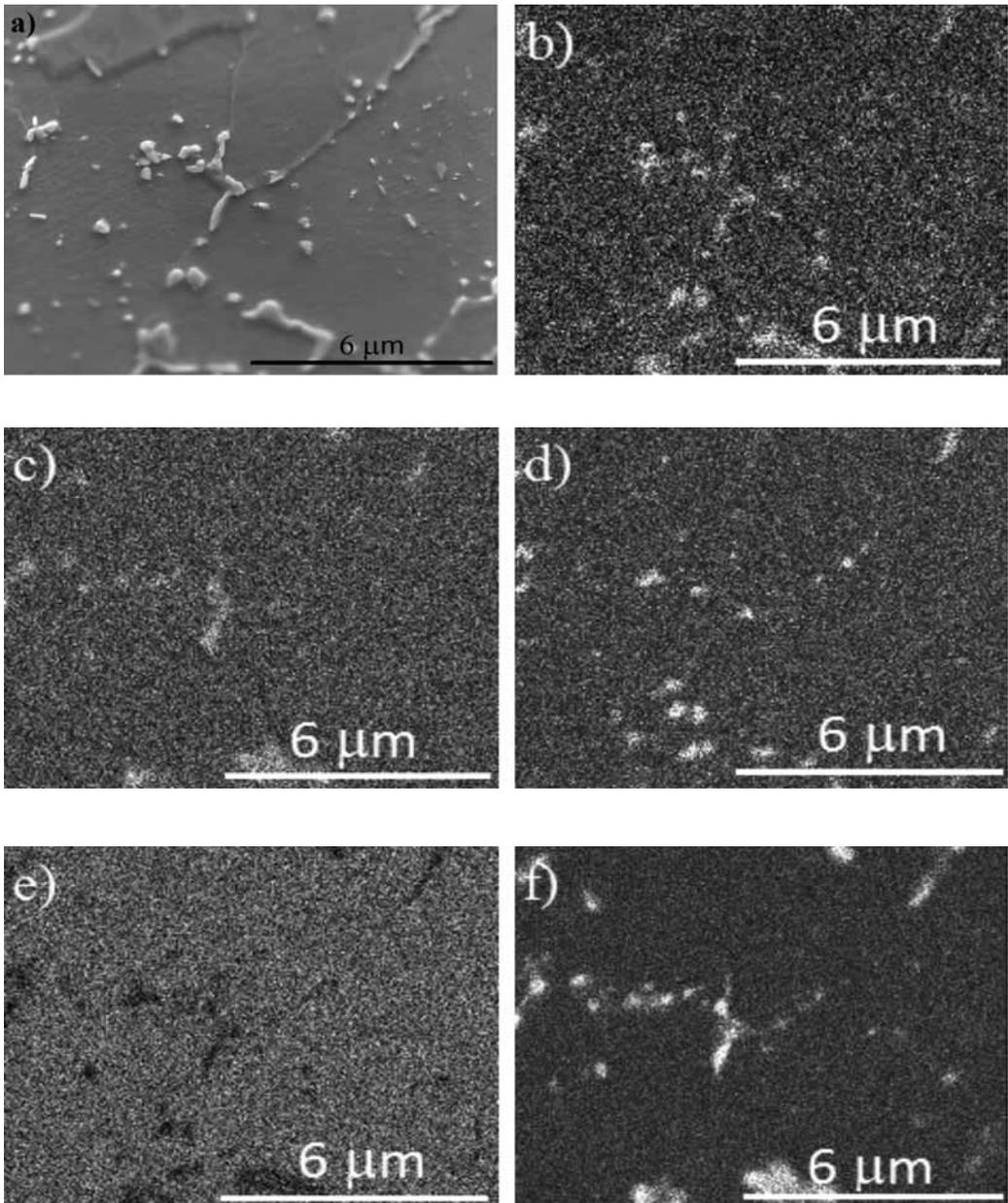


Figure 10. Element distribution from EDXS: a) SE Image, b) C, K α ; c) Si, K α ; d) Cr, K α ; e) Fe, K α ; f) Mo, L α .

CONCLUSIONS

In this paper the application of Auger electron spectroscopy (AES) and energy dispersive x-ray spectroscopy (EDXS) were presented for characterization of carbide precipitates in modified 9 % Cr steel. AES is a surface sensitive technique, while EDXS is not. The Auger electrons come from the top few atomic layers of the surface (0.5–5 nm), while characteristic x-rays from 1–3 μm , depends on the accelerating voltage of incident electron beam and material density. AES showed that the precipitates contain C, Fe, Cr and Mo which was also confirmed by EDXS analyses. AES measurement of C line shape showed that the carbon in the precipitates was present as carbide. Carbide precipitates were not homogeneous but were mixed iron-chromium-molybdenum carbides. Silicon enrichment close to the carbide precipitate/matrix interfaces was also observed. In the case of EDXS analysis of the precipitates the results obtained by lower accelerating voltage of incident beam (10 kV) were much better since less x-rays come from the matrix. However, for the determination of the types of carbides other techniques, such as diffraction techniques (TEM, XRD, EBSD) should be used.

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