

EVALUATION OF THE STRUCTURAL CHANGES IN 9 % Cr CREEP-RESISTANT STEEL USING AN ELECTROCHEMICAL TECHNIQUE

OCENA SPREMEMB STRUKTURE V JEKLU Z 9 % Cr, ODPORNEM PROTI LEZENJU, Z UPORABO ELEKTROKEMIJSKE TEHNIKE

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A correct prediction of the remaining lifetime of the components for power plants requires an evaluation of the material structural stability. In this work, the possibility of a non-destructive evaluation of the structural changes in 9 % Cr creep-resistant steel P92 after a long-term annealing was investigated using the electrochemical-polarization technique. Aging at 650 °C caused a significant precipitation and coarsening processes resulting in a redistribution of some alloying elements in the structure. The structural changes confirmed by scanning-electron-microscopy observations and a hardness measurement affected the shape of the measured potentiodynamic curves. Significant local peaks on this curve, in the active-to-passive transition area and in the transpassive region, were evaluated. Characteristic current densities in these regions showed very good correlation with the results of the structure observation and hardness testing.

Keywords: 9 % Cr creep-resistant steel, structural changes, electrochemical detection, polarization curve

Pravilna napoved preostale trajnostne dobe komponent v termoelektrarnah zahteva oceno stabilnosti strukture materiala. V tem delu je bila preiskovana možnost neporušne ocene sprememb v strukturi jekla z 9 % Cr, odpornega proti lezenju, z uporabo tehnike elektrokemijske polarizacije. Staranje pri 650 °C je povzročilo močno izločanje in procese rasti, kar je povzročilo prerazporeditev nekaterih legirnih elementov v strukturi. Spremembe v strukturi, potrjene pri opazovanju z vrstičnim elektronskim mikroskopom in pri merjenju trdote, so vplivale na obliko izmerjenih potenciodinamičnih krivulj. Ocenjeni so bili lokalni vrhovi na tej krivulji v območju prehoda iz aktivnega v pasivno in v transpasivnem območju. Značilna gostota tokov v teh območjih je pokazala dobro ujemanje z rezultati opazovanja strukture in z meritvami trdote.

Ključne besede: jeklo z 9 % Cr, odporno proti lezenju, spremembe strukture, elektrokemična detekcija, polarizacijska krivulja

1 INTRODUCTION

Modified steel with 9 % Cr P92 (9Cr-0.5Mo-1.8W-V-Nb) is nowadays often used for the structural components of power plants working under creep conditions (rotors, turbine blades, tubing).¹⁻³ A combination of a specific chemical composition and a suitable heat treatment provides these materials with a creep strength of up to 100 MPa at 600 °C (after 10⁵ h) or even higher.⁴ Their operation temperature is limited to about 620 °C; however, the possibilities of increasing it up to 650 °C are being studied. The limiting factor is their poor steam-oxidation resistance and also the acceleration of undesirable structural changes under these conditions.

The structure of the P92 steel after quenching and tempering consists of tempered martensite with a high dislocation density (10¹³–10¹⁴ m⁻²).⁵ The martensite laths and the former austenite grain boundaries are decorated with chromium-rich carbides M₂₃C₆, while the grain itself contains finely dispersed particles of the MX type (M = V, Nb, X = C, N). This structure provides the necessary creep resistance. Nevertheless, a long-term

exposure causes a coarsening or decomposition of some particles and the formation of new phases.⁶ The phase with the highest effect on the creep properties is the Laves phase with the (Fe,Cr)₂(Mo,W) formula, since it drains the structure of the solid-solution strengthening elements (Mo, W).⁷ These phenomena significantly decrease the creep strength, the ductility, the corrosion and the oxidation resistance.

A correct prediction of the remaining lifetime of a component requires a quantification of these structural changes. Commonly, the mechanical attributes (the hardness, the tensile strength or the fracture toughness) are measured and compared to the initial values. Despite providing direct information about the mechanical attributes of a material, such testing requires samples of the studied component material; the component is cut into test samples, thus losing its function. Therefore, non-destructive methods providing similar quality information are being explored. For instance, electrochemical polarization provides an interesting method based on the change in the corrosion behavior of a material due to the

Table 1: Chemical composition of steel P92 in mass fractions (w/%)

Tabela 1: Kemijska sestava jekla P92 v masnih deležih (w/%)

C	Mn	Si	Cr	Ni	Mo	W	V	Nb	N	B
0.11	0.48	0.37	8.6	0.09	0.33	1.6	0.23	0.06	0.037	0.0025

phases formed during the exposure.⁸⁻¹¹ The particles formed in the structure during the operation are, as mentioned above, rich in some alloying elements (Cr, Mo and W)¹² – all these elements dissolve in highly oxidative environments due to the transpassive mechanism.¹³ A preferential dissolution of these phases alters the common steel polarization curve. In addition, electrochemical polarization could be utilized as a method complementary to the small-sample testing.¹⁴ A previous study¹⁵ suggests a possible utilization of the steel behavior in the transpassive region for detection purposes. This study deals with an evaluation of steel P92 after different heat treatments/long-term exposures using polarization techniques.

2 EXPERIMENT

The chemical composition of the P92 steel is shown in **Table 1**. The samples were in the state after a heat treatment or after a long-term exposure. **Table 2** shows their thermal histories.

The structures of the samples were studied using light microscope Olympus PME3 and scanning electron microscope Tescan Vega 3 equipped with an EDS probe. The samples were paper ground up to the P2500

Table 2: Thermal treatment

Tabela 2: Termična obdelava

Denomination	Thermal history
Q	quenched (1050 °C / water)
QT	quenched and tempered (780 °C / 120 min)
A1	annealed at 650 °C for 1 h
A2	annealed at 650 °C for 10 h
A3	annealed at 650 °C for 100 h
A4	annealed at 650 °C for 1000 h
A5	annealed at 650 °C for 8000 h
A6	annealed at 650 °C for 15000 h
A7	annealed at 650 °C for 20000 h

roughness, polished with a diamond paste and etched in a mixture of 5 % Nital and Vilella-Bain (1:1). The chemical composition was determined using an EDS analyzer. The hardness of the samples was measured on the polished samples using the standard Vickers method with an applied load of 1 kg; the loading time was 10 s. The hardness of each sample was calculated from ten measurements.

The samples for the potentiodynamic measurements were first ground on a rotating disc with the abrasive paper with a roughness of up to P600. The potentiodynamic measurements were conducted in a corrosion cell

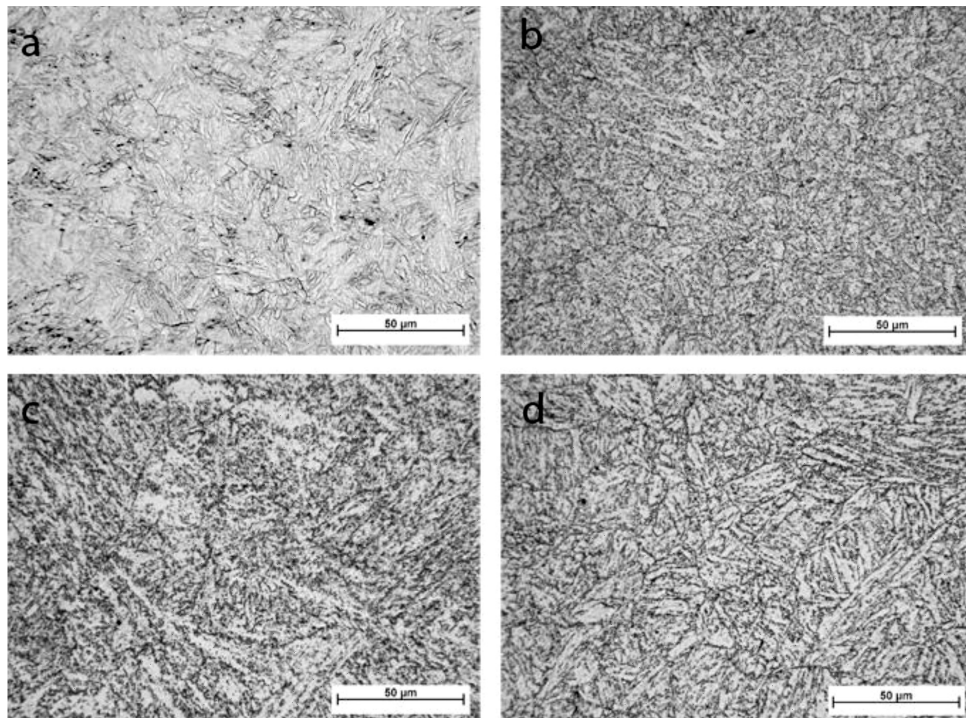


Figure 1: Microstructures of the samples: a) Q, b) QT, c) A4, d) A6

Slika 1: Mikrostruktura vzorcev: a) Q, b) QT, c) A4, d) A6

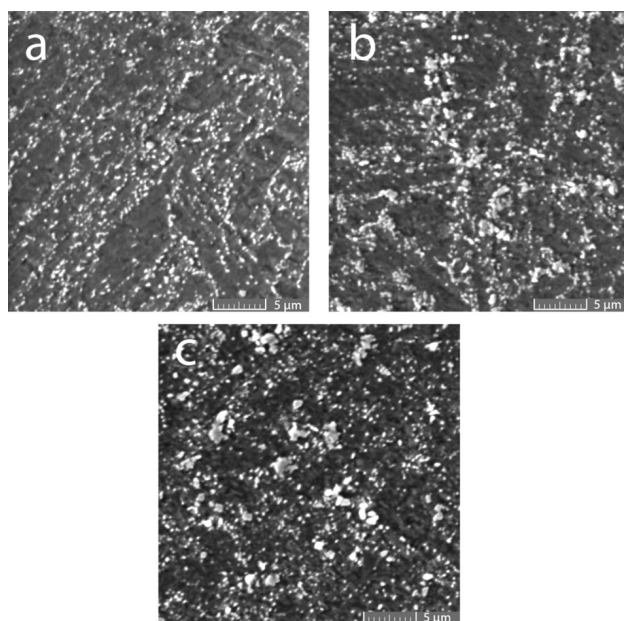


Figure 2: SEM images of the samples: a) A2, b) A4, c) A7
Slika 2: SEM-posnetki vzorcev: a) A2, b) A4, c) A7

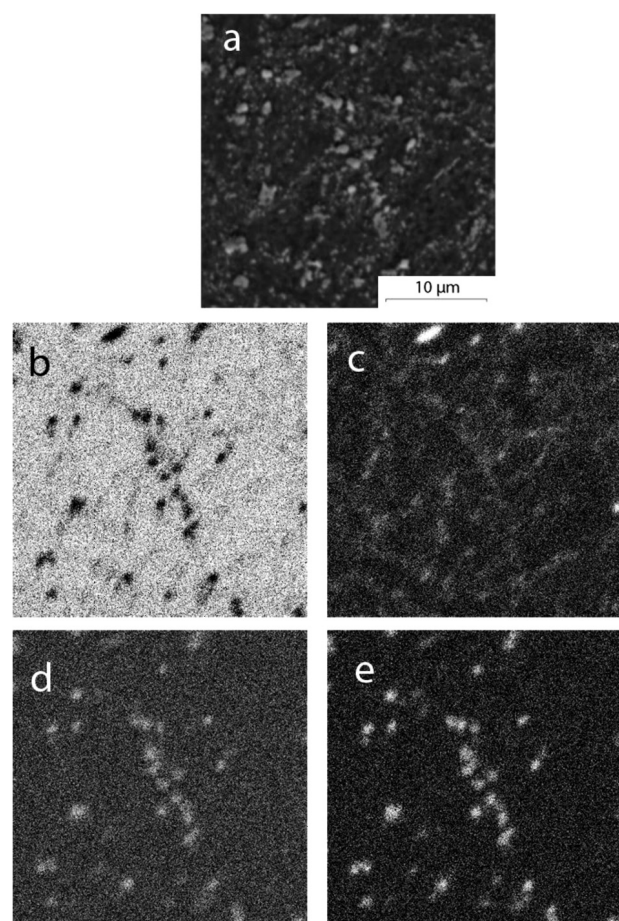


Figure 3: a) SEM image of sample A7; element maps for: b) Fe, c) Cr, d) Mo, e) W

Slika 3: a) SEM-posnetek vzorca A7; razporeditev elementov: b) Fe, c) Cr, d) Mo, e) W

with the classical three-electrode set-up with the sample being connected as the working electrode, a platinum wire as the auxiliary electrode and saturated silver/silver chloride as the reference electrode. The electrolyte was a solution of sulphuric acid of a 0.5 mol L^{-1} concentration at ambient temperature. The measurement consisted of corrosion potential stabilization for 15 min, immediately followed by a polarization from cathodic region -0.05 V , E_{corr} up to 1.8 V . The sweep rate was 2 mV s^{-1} . Potentiostat Gamry PC3 connected to a computer with a Gamry Instruments program was used in all the measurements. The polarization curves for samples A1-A7 were measured three times and the average values of the evaluated parameters were determined. All the presented data are related to the reference electrode described above.

3 RESULTS AND DISCUSSION

The microstructures of the selected samples are shown in **Figure 1**. The structure of the quenched sample (Q) consists of martensitic lath-shaped grains without any distinctive precipitates. The tempered sample (QT) has the desired structure of tempered martensite with fine precipitates on the former austenitic grain boundaries and martensitic lathes. The long-term annealing at 650 °C resulted in the coarsening of the grains (A4, A6), the phases and also in the formation of new particles.

Detailed structures are visible on the pictures obtained with scanning electron microscope (**Figure 2**). After about 1000 h of the exposure at 650 °C large precipitates form in the structure (sample A4); their size slowly increases with further annealing (A7). These particles were identified as a Laves phase rich in Mo and

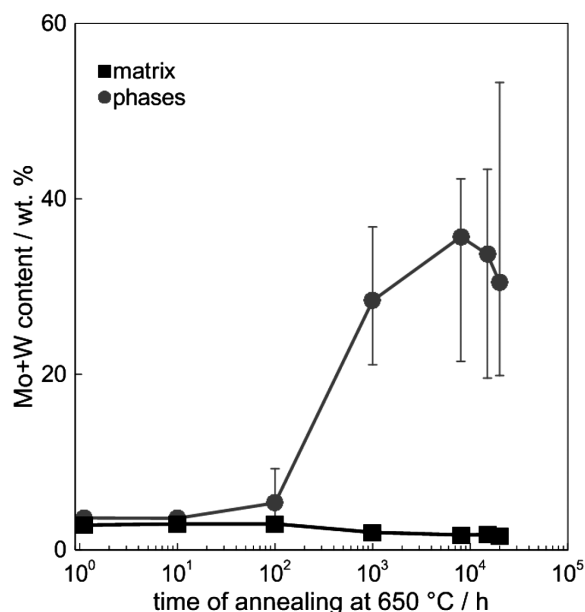


Figure 4: Effect of annealing on Mo+W content in matrix and in phases

Slika 4: Vpliv žarjenja na vsebnost Mo+W v osnovi in v fazah

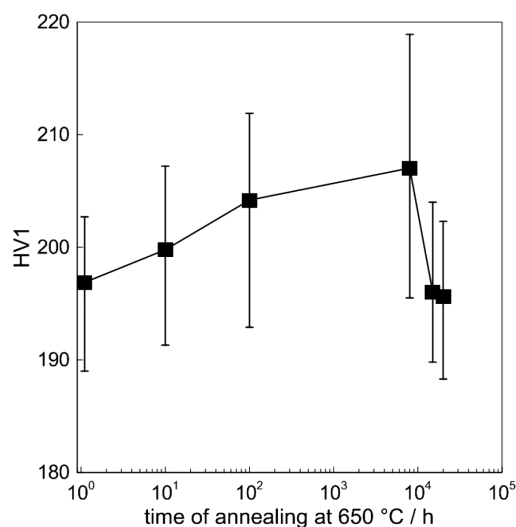


Figure 5: Effect of annealing on hardness
Slika 5: Vpliv žarjenja na trdoto

W; the precipitation of this phase in the 9 % Cr steel was described by several authors.¹⁻⁷ The phase composition was verified by element mapping (Figure 3). It is apparent that the observed phases contain high amounts of both tungsten and molybdenum, while the chromium content is reduced compared to the surrounding material. In addition, the phases contain only very little iron.

Figure 4 shows the effect of the annealing time on the contents of molybdenum and tungsten in the forming phases and the adjacent matrix (determined from the EDS analysis). The element contents in the phases increase abruptly after 1000 h of the annealing, but further annealing has no significant effect. On the other hand, the contents of these elements in the matrix slowly decrease during the annealing. A decrease in the Mo and W contents during the operational exposure is well known^{4,6} and it results in a decrease in the solid-solution strengthening and, thus, a reduction in the creep resistance.

The effect of the structural changes on the mechanical properties was verified with a hardness measurement (a load 1 kg). The average hardness of the quenched sample was 351 HV1, the tempering resulted in a decrease of this value, to 188 HV1. The effect of the subsequent annealing of the material is shown in Figure 5. It can be clearly seen that the hardness increases during the initial stages, probably due to the hardening processes occurring in the structure. The precipitation of the finely dispersed MX particles is assumed to be the most significant hardening process in the structure. Sample A5 (after 8000 h of annealing) has the highest hardness of 207 HV1. Further annealing at 650 °C causes a deterioration in the hardness, most likely due to the carbide coarsening and the formation of a brittle Laves phase.¹⁰ While a decrease in the hardness was observed after the annealing for 15000 h (A6), the W- and Mo-rich phases were detected already after 1000 h

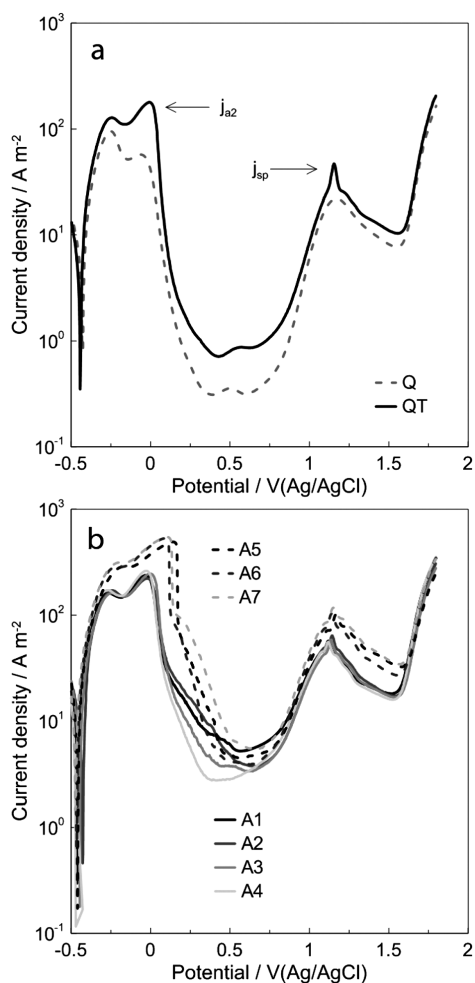


Figure 6: Potentiodynamic curves of samples: a) Q and QT, b) A1–A7
Slika 6: Potenciodinamične krivulje vzorcev: a) Q in QT, b) A1–A7

(A4) (Figure 4). This discrepancy can be explained with the fact that the change in the hardness is not associated only with the precipitation of the W- and Mo-rich phases, but it is caused by many structural changes (the changes in the dislocation density, the coarsening of the $M_{23}C_6$ particles, the precipitation of the MX particles).

An enrichment or formation of the phases with a high content of an alloying element was used for assessing the material with the electrochemical-polarization method. The typical polarization curves for the P92 steel quenched and tempered in a 0.5 mol L⁻¹ sulphuric acid are shown in Figure 6a. The active/passive transient on the curve exhibits itself as a second anodic maximum (the peak labeled as j_{a2}). The transpassive-dissolution/secondary-passivity region is characterized by the local peak around the 1.25 V potential with current density j_{sp} . It is obvious from the plots that the tempering increases the current density of both the second anodic peak j_{a2} and the transpassive peak j_{sp} . The potentiodynamic curves of the annealed steel samples are shown in Figure 6b. The shape of these curves does not change, only the current-density levels in the studied regions increase.

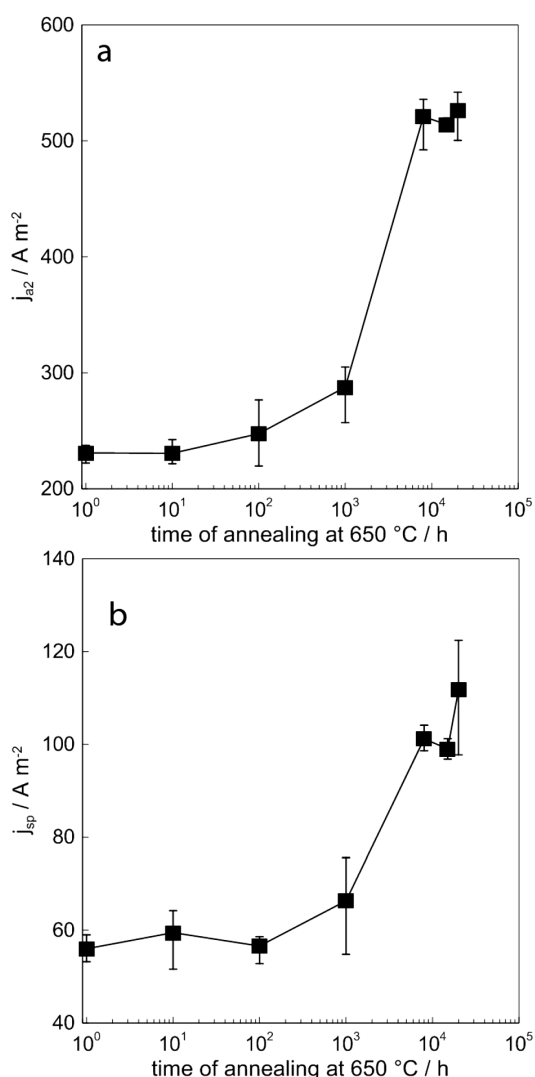


Figure 7: Effect of annealing at 650 °C on potentiodynamic-curve attributes: a) j_{a2} , b) j_{sp}
Slika 7: Vpliv žarjenja pri 650 °C na značilnosti potenciodinamičnih krivulj: a) j_{a2} , b) j_{sp}

The increase in the second anodic peak was discussed in many papers^{16,17} and it is presumed that this effect corresponds to the formation of chromium-depleted regions around the $M_{23}C_6$ carbides. The chromium content in carbides increases with further annealing which also significantly depletes the adjacent regions of chromium, resulting in an increase in the j_{a2} peak current density.

A similar trend was observed for the j_{sp} peaks at 1.25 V, where the current density also increases with the annealing time. This phenomenon can be explained with an increase in the number of minor phases rich with Cr, Mo and W, which can dissolve due to the transpassive mechanism at this potential. Chromium has the greatest effect on this phenomenon and it is known that its content in $M_{23}C_6$ increases with the annealing time.¹² However, the effects of Mo and W in the Laves phases cannot be ignored, as shown in **Figure 4**. The relationships bet-

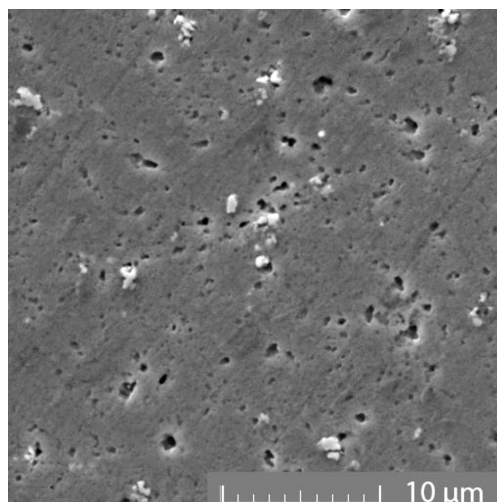


Figure 8: SEM image of the A7 sample after potentiostatic etching (1.25 V)
Slika 8: SEM-posnetek vzorca A7 po potenciostatičnem jedkanju (1,25 V)

ween j_{sp} , j_{a2} and the annealing time are shown in **Figure 7**. Both these characteristics increase significantly after 8000 h and remain stable afterwards. In addition, it is necessary to emphasize that a sharp increase in j_{sp} corresponds to an intensive active dissolution of the matrix, therefore, increasing the area of the phases that are dissolved in the transpassive state at 1.25 V.

The observed trends between j_{a2} , j_{sp} and the annealing time are in a good correlation with the hardness measurements, which also change significantly after 8000 h. The Laves phase starts to precipitate soon, after 1000 h (**Figure 2**), so it seems that the increase in the j_{sp} value corresponds mostly to the change in the $M_{23}C_6$ chemical composition. To prove that the phases are being dissolved at 1.25 V, sample A7 was briefly potentiostatically etched. **Figure 8** shows a SEM image and it is clear that some phases in the matrix are partially dissolved.

4 CONCLUSION

The recording of potentiodynamic curves in sulphuric acid seems to be an interesting method to assess the structural changes in creep-resistant steel P92. Two parts of the polarization curves were studied in detail – the second anodic peak in the active/passive transient region and the local-current maximum in the transpassive region. Both these peaks correspond to the changes in the structure during a long-term annealing and these further correlate with the hardness measurements. Therefore, the utilized polarization method is sensitive to both the behavior of the matrix (j_{a2}) and the changes in secondary phases in the matrix (j_{sp}). Due to its simplicity and non-destructivity, the electrochemical-polarization method could be an attractive choice when predicting the remaining lifetime of operating equipment.

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