INTERFACIAL STUDY OF 19Cr-13Ni AUSTENITIC STAINLESS STEEL AFTER HOLDING AT ELEVATED TEMPERATURES

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The paper presents the results of interfacial studies of 19Cr-13Ni austenitic stainless steel doped with 0.26 mass % phosphorus after annealing at 700 and 800 °C for 100 and 1000 h by means of high resolution Auger electron spectroscopy (HRAES). After annealing for 100 h the lower than equilibrium concentration of phosphorus at grain boundaries was revealed. The P-S site competition effect was considered as a possible reason of this phenomenon. The local increase of phosphorus grain boundary concentration above the equilibrium level after annealing for 1000 h at both temperatures was attributed to the presence of Cr, P-rich particles (probably chromium phosphides).

Key words: austenitic steel, grain boundary segregation, phosphorus, sulfur, High Resolution Auger Electron Spectroscopy (HRAES)

MIKROCHEMICKÉ ŠTÚDIUM 19Cr-13Ni AUSTENITICKEJ NEHRDZAVEJÚCEJ OCELE PO VÝDRŽI PRI ZVÝŠENÝCH TEPLOTÁCH

V článku sú prezentované výsledky štúdia 19Cr-13Ni nehrdzavejúcej austenitickej ocele s hmotnostným obsahom fosforu 0,26 % po výdrži 100 a 1000 h pri teplotách 700 a 800 °C metódou Augerovej elektrónovej spektroskopie. Po 100 h sme na hraniciach zŕn zistili nižší obsah fosforu, ako je rovnovážna koncentrácia, čo možno vysvetliť ako dôsledok pôsobenia konkurenčného efektu P-S. Po 1000 h výdrže je koncentrácia fosforu v lokálnych oblastiach hraníc zŕn vyššia, ako je rovnovážna koncentrácia v dôsledku precipitácie častíc bohatých na Cr a P.

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1. Introduction

Cr-Ni austenitic stainless steels are widely used in power plants and chemical industry because of their good mechanical properties and corrosion resistance at elevated temperatures [1]. One of the most important factors influencing the reliability of austenitic steels in high-temperature structural applications is the chemistry of grain boundaries [2]. Microchemical changes near grain boundaries can evoke the sensitization of austenitic steels to intergranular corrosion and stress corrosion cracking [2–8]. Even if the formation of chromium depletion zones due to the precipitation of intergranular $M_{23}C_6$ particles is the decisive microchemical mechanism of sensitization, the grain boundary segregation of impurities (e.g. phosphorus) can also contribute to this process [9–12].

The role of phosphorus in affecting the mechanical, fracture, and corrosion properties of austenitic steels during long-term high temperature exposures was intensively studied in the last decades [9–23]. Banerjee et al. [13] stated that phosphorus favors the nucleation of $M_{23}C_6$ particles at grain boundaries and $\{111\}$ matrix planes, but retards their growth. Disperse $M_{23}C_6$ particles formed due to the higher phosphorus occurrence stabilize the dislocation substructure and restrain from restoring the original microstructure, e.g. after cold working. Phosphorus was also found to delay the formation of intermetallic phases [20]. Briant et al. [3, 14, 15] confirmed the competitive segregation of phosphorus, nitrogen, and sulfur. Bruemmer [2], Ortner [16], and Ilyin [17] have investigated microchemical changes at grain boundaries during isothermal exposures. They found out that sensitized austenitic steels (containing chromium depletion zones along grain boundaries due to the $M_{23}C_6$ precipitation [5–7]) are more convenient for the phosphorus segregation than non-sensitized ones. The replacement of carbon and chromium with phosphorus and sulfur in chromium depletion zones of 16Cr-15Ni-3Mo-1Nb steel was reported by Ilyin [17].

In the previous paper [23] the influence of annealing conditions on changes in phosphorus grain boundary concentration, size of intergranular particles, and carbide coverage at grain boundaries in 18Cr-12Ni austenitic steel was investigated. It was shown that the equilibrium values of phosphorus grain boundary concentration closely correlate with the values of weight loss (penetration depth) measured by means of Huye test.

Recently, the thermodynamic parameters of phosphorus grain boundary segregation for polycrystalline 17Cr-12Ni austenitic steel were determined [24]. The less negative value of phosphorus segregation enthalpy, -14.1 kJ/mol, indicates the presence of rather special than general grain boundaries in the steel.

In the present paper results of HRAES (High Resolution Auger Electron Spectroscopy) studies for 19Cr-13Ni austenitic stainless steel doped with 0.26 mass % phosphorus are reported.

2. Experimental

Chemical composition of the investigated steel is given in Table 1. The steel heat treatment consisted of annealing at 1100 ℃ for 20 h, water cooling, annealing at 700 ℃ and 800 ℃ for 100 h and 1000 h, and water cooling.

Table 1. Chemical composition of the investigated steel

	C	Si	Mn	P	Cu	S	Cr	Mo	Ni	V	Ti	Co
Mass %	0.084	0.11	0.08	0.260	0.04	0.007	19.7	0.010	13.3	0.04	< 0.01	0.03
Atomic %	0.385	0.24	0.08	0.462	0.03	0.012	20.8	0.006	12.5	0.04	< 0.01	0.03

Auger electron spectra were obtained by means of high resolution Auger electron spectrometer with field emission electron source VG Microlab 310-F. The analyses were performed in microprobe under UHV (Ultra High Vacuum) of 10^{-8} Pa. Parameters of primary electron beam were: 10 keV (energy), 10 nA (current), and 10 nm (approximate beam diameter). Cylindrical notched specimens with diameter of 5 mm and length of 30 mm were impact-fractured at −120 ℃ *in situ*. Intergranular and transgranular facets on freshly prepared fracture surfaces were immediately observed and analyzed. The data recorded in integral mode were numerically derived and smoothed by means of the fast Fourier transformation method [25].

3. Results

On fracture surfaces two types of facets were observed: intergranular ones with dimple morphology (Figs. 1a, 2a) and transgranular cleavage-like ones (Fig. 3a). On intergranular facets number of inclusions was found (Fig. 4a). Typical AES spectra corresponding to different fracture surfaces are shown in Figs. 1–5. The grains (average size of 256 μm) formed during the solution heat treatment were found to be large enough for satisfactory analysis of observed facets. The AES spectra contained peaks of Fe, Cr, C, P, S, and O. An occurrence of the oxygen peak in all Auger spectra was caused by adsorption from residual atmosphere or by presence of oxide inclusions on intergranular facets.

4. Discussion

Intergranular facets with dimple morphology dominate on fracture surfaces of all samples investigated (Figs. 1a, 2a). In agreement with Ref. [19] the portion of intergranular fracture increases with increasing annealing time and temperature. This phenomenon was attributed to the size of intergranular $M_{23}C_6$ particles proportional to annealing conditions [26]. The higher annealing temperature and/or

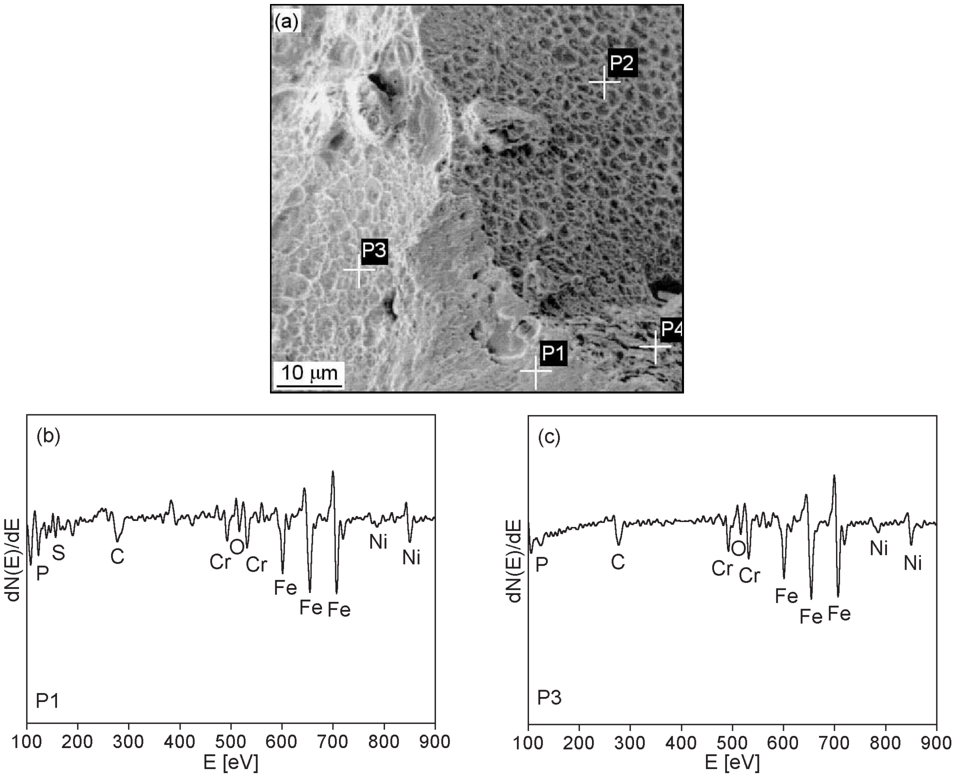

Fig. 1. Intergranular facets on fracture surface of sample aged at 700 °C for 1000 h: (a) SEM image, (b) Auger spectrum measured in P1 with higher P level, (c) Auger spectrum measured in P3 with lower P level.

longer annealing time, the larger intergranular particles. As shown in Ref. [27], there is a positive correlation between the size of the particles and the susceptibility of the steel to intercrystalline embrittlement. The presence of inclusions at grain boundaries can also contribute to the intergranular failure. With respect to the annealing conditions applied, a high portion of intergranular fracture in the investigated steel is in agreement with the theoretical expectation [19].

The obtained Auger spectra were not corrected with respect to the signals arising from precipitates. Thus, the experimentally determined grain boundary concentrations of individual elements [28, 29] do not reflect true segregated levels. They are, for instance, about 6 and 20 at. % for the conditions annealed at 800 °C for 100 h and 1000 h, respectively. The calculated equilibrium value of phosphorus grain boundary concentration (according to [24]) at 800 °C is about 12 at. %. The comparison of calculated and experimentally determined values indicates that annealing for 100 h is not sufficiently long to reach the equilibrium level of phospho-

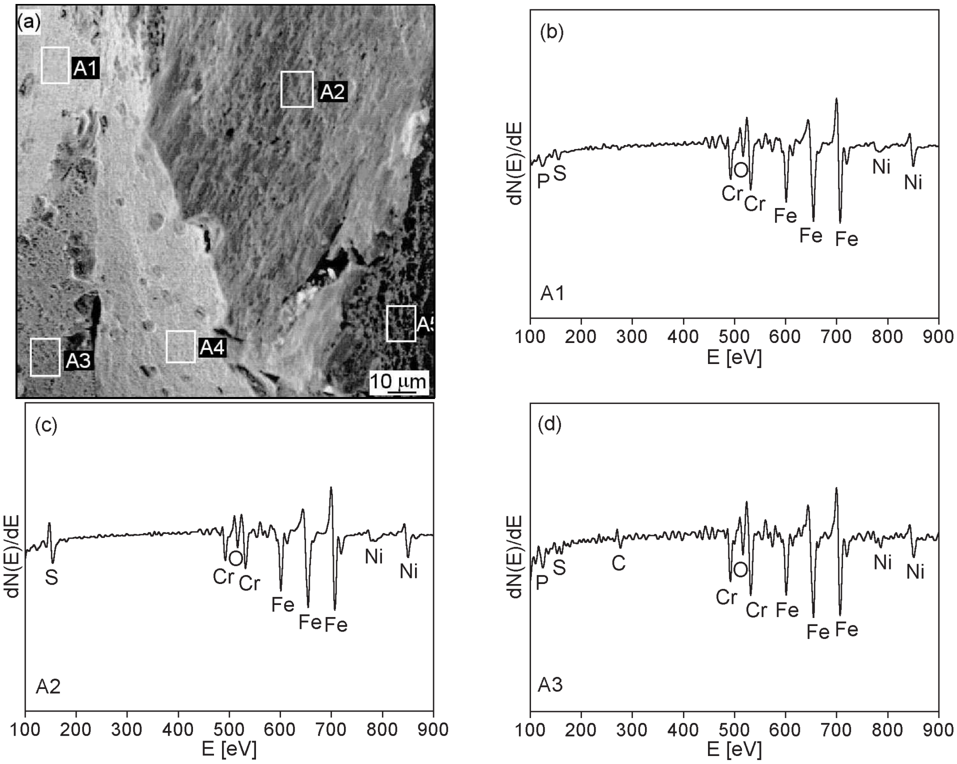

Fig. 2. Intergranular facets on fracture surface of sample aged at 800 °C for 100 h: (a) SEM image, (b) Auger spectrum of area A1 with segregated P and S, (c) Auger spectrum of area A2 with S occurrence only, (d) Auger spectrum of area A3 with peaks of P, S, and C.

rus. On the other hand, after 1000 h of annealing the experimentally determined value (20 at. %) exceeds the calculated one (12 at. %). The concentration of individual segregated elements would match well the measure of the segregation at free surface, however, it is too high for grain boundary segregation. There is a question, how to explain the above differences?

The AES measurements confirmed a non-uniform distribution of phosphorus on analyzed fracture surfaces. For instance, the high phosphorus peaks were observed on transgranular facets only locally (Figs. 3b,c). On intergranular facets, higher phosphorus peaks were recorded, if analyzed an intergranular particle (Figs. 5b,c). Additional measurements in close neighborhood of the particle revealed only negligible phosphorus content (Fig. 5d). The reduction of phosphorus concentration in surrounding of the particle can be caused by phosphorus drawing into the particle during its growth. The phosphorus content in analyzed areas correlated positively with chromium content (Figs. 3b,c, 4d, 5b,c). All the mentioned

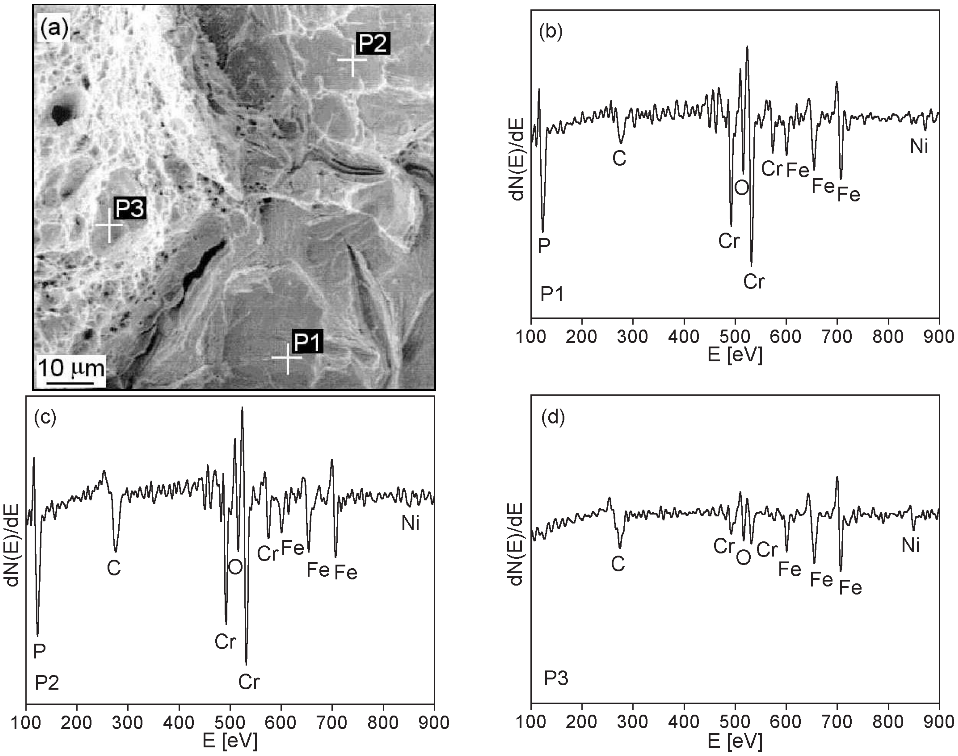

Fig. 3. Transgranular facets on fracture surface of sample aged at 800 °C for 1000 h: (a) SEM image, (b) Auger spectrum of P1 with high P and Cr peaks, (c) Auger spectrum of P2 with high P, C, and Cr peaks, (d) Auger spectrum of P3 with high C peak.

facts indicate Cr, P-rich particles (e.g. phosphides) precipitated at grain boundaries and/or in the grain interior. The higher phosphorus peaks and corresponding grain boundary concentrations of phosphorus in the condition annealed for 1000 h at 800 °C can arise from the combined effects of phosphorus segregation and phosphide precipitation. Phosphorus-rich inclusions with higher levels of Cr and Si were also observed by Li and Messler [18] in 19Cr-11Ni austenitic steels. Janovec and Grabke [30] reported the occurrence of $M_{3\text{-}4}P$ and CrFeP phosphides at grain boundaries in 16Cr-0.11Ni ferritic steels. The latter authors proposed also a simple criterion for the prediction of intergranular phosphide precipitation. If the value of the $(C+N)/P$ ratio (C, N, and P are bulk contents of C, N, and P, respectively, in at. %) is lower than 13, phosphides would precipitate. Application of the criterion to the 19Cr-11Ni steel with 0.027 % P [18] (value of the $(C+N)/P$ ratio is 9.7) tends to a good agreement with the results of experimental measurements. For the investigated steel, the $(C+N)/P$ ratio is extremely low (0.83) what indicates the

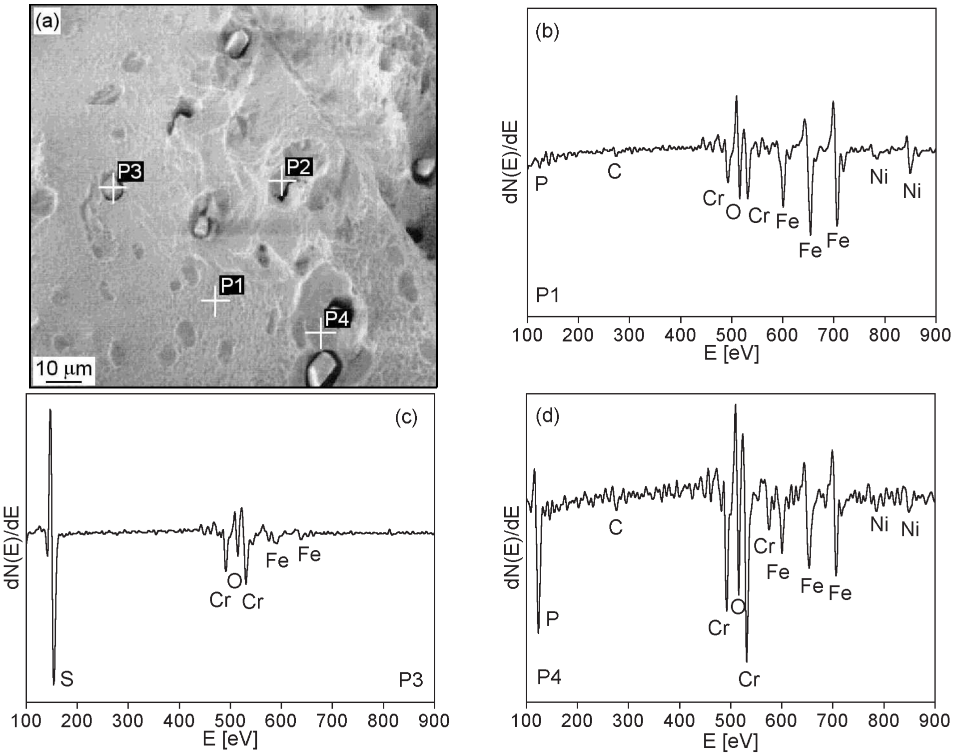

Fig. 4. Intergranular facet on fracture surface of sample annealed at 800 °C for 100 h: (a) SEM image, (b) Auger spectrum of P1 with low P and C peaks, (c) Auger spectrum of P3 with high S peak, (d) Auger spectrum of P4 with high P and Cr peaks.

highest probability of the phosphide precipitation. It can also be interpreted as an indirect theoretical evidence for the phosphide occurrence in the investigated steel.

In conditions annealed for 100 h, phosphorus peaks were accompanied by sulfur ones (Figs. 2b,d). This indicates phosphorus and sulfur can compete for convenient sites at grain boundaries. The P-S site competition effect [3, 14, 15] could also cause in the above conditions a decrease of the phosphorus grain boundary concentration below the equilibrium level estimated by means of thermodynamic calculations [24]. The reason for this consists in the higher diffusion rate of sulfur (2.3×10^{-11} cm^2/s at 800 °C [31]) in comparison to the phosphorus (6.8×10^{-12} cm^2/s at 800 °C [21]). During short-term annealing (100 h), sulfur segregates firstly to grain boundaries, then it is built in Cr-rich sapphires (Fig. 4c) [15]. After long-term annealing sulfur is replaced by phosphorus (Fig. 4d).

The results introduced in the present work confirmed the formation of P-rich particles (probably chromium phosphides) in the investigated steel. The indirect

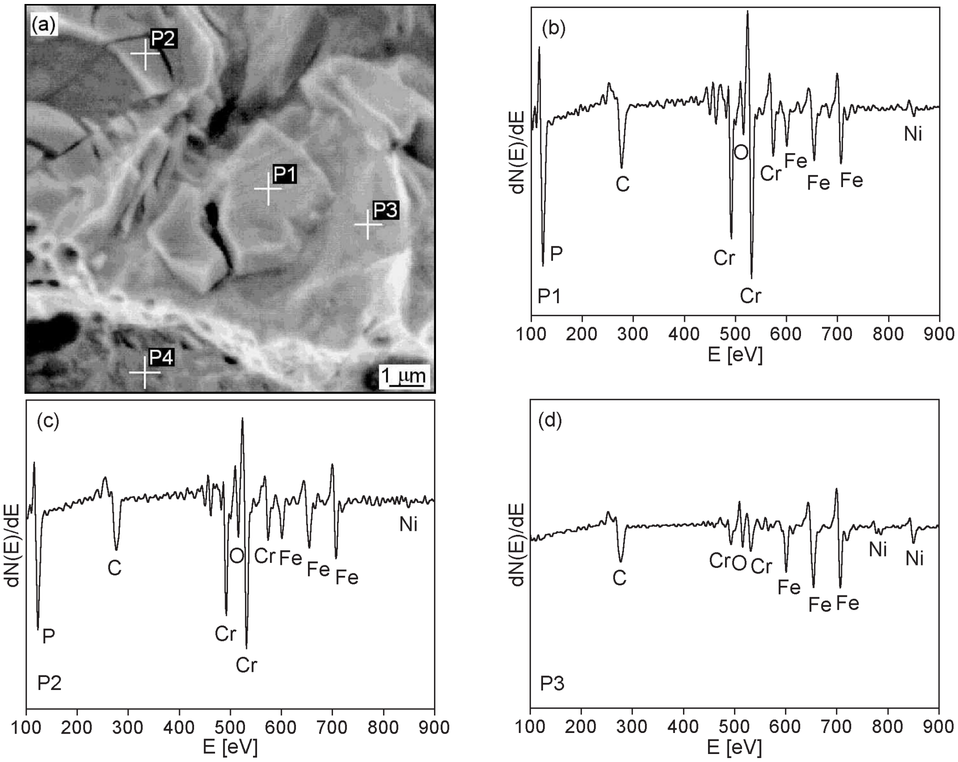

Fig. 5. Intergranular facet on fracture surface of sample aged at 800 °C for 1000 h: (a) SEM image of intergranular particles, (b) Auger spectrum of particle P1 showing high P, C, and Cr peaks, (c) Auger spectrum of particle P2 showing high P, C, and Cr peaks, (d) Auger spectrum of P3 with missing P and Cr peaks.

evidence for the P-S site competition effect was also given. To complete the presented results, TEM analysis of the type and chemical composition of intergranular particles will be done in the near future.

5. Conclusions

The results of the interfacial analysis (by means of Auger electron spectroscopy) of the 19Cr-13Ni austenitic stainless steel doped with 0.26 mass % of phosphorus after annealing at both 700 and 800 ℃ for 100 and 1000 h can be concluded as follows:

1. Intergranular ductile fracture was found to be the prevalent fracture mechanism of samples impact fractured at −120 ℃.

2. Both, sulfur-rich and phosphorus-rich particles were observed on fracture surfaces analyzed.

3. After annealing for 1000 h at both temperatures phosphorus was non-uniformly distributed along grain boundaries. The local increase of phosphorus grain boundary concentration above the equilibrium level was attributed to the presence of Cr, P-rich particles (probably chromium phosphides).

4. The conditions annealed for 100 h revealed lower than equilibrium concentration of phosphorus at grain boundaries. The P-S site competition effect was considered as a possible reason of this phenomenon.

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