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INTERDIFFUSION STUDY IN THE SYSTEM Ni—Fe_3O_4

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Diffusion processes in the system Ni—Fe_3O_4 *were studied between 900 and 1300 °C in controlled atmosphere using electron probe X-ray microanalysis. The values of diffusion coefficients of nickel in magnetite were determined in the temperature range from 900 to 1100 °C. The activation energy of the diffusion was found* 2.6×10^2 *kJ mol*$^{-1}$. *Formation of a three-phase reaction product consisting of spinel* [$Ni_xFe_{3-x}O_4$], *wüstite* [(Ni, Fe) 0] *and metal* [(Ni, Fe)] *was observed in the temperature range from 1150 to 1300 °C.*

INTRODUCTION

The system Fe—Ni—O belongs among the ferrite-forming systems. Nickel ferrite constitutes the basic component of numerous commercial magnetic materials. The phase equilibria and the diffusion coefficients in the given system should form the basis of qualified considerations of synthesis of these ferrites by means of ceramic processes, as well as of considerations concerning the production of nickel from laterite ores. In spite of the considerable attention which has been paid to this field in the last two decades, the available data on phase equilibria in the given system are frequently incomplete and controversial.

No adequate survey of results has so far been published in literature as concerns the diffusion processes in technologically significant systems of the type metal-oxide. The diffusion mechanism involved has also not been subjected to any detailed theoretical analysis. The diffusion processes taking place in the system Ni—Fe_3O_4 have not yet been studied. For the purposes of comparison use can only be made of the results obtained in the study of self-diffusion of Fe in Fe_3O_4 [1]—[3] or that of Ni in $Ni_xFe_{3-x}O_4$ for various Fe/Ni ratios (2.1, 2.5, 3.5, 7) [4].

The present study had the aim to investigate the interaction of nickel metal with magnetite from the point of view of chemical and phase composition of the respective products, and to determine the diffusion coefficients of Ni^{2+} in magnetite.

EXPERIMENTAL PROCEDURE

The diffusion processes were studied by the sandwich arrangement of the samples using nickel-coated magnetite mineral plates 12×8×3 mm in size. Polycrystaline natural magnetite was used as the Fe_3O_4. The hickness of the nickel plate was 2 mm.

The diffusion couples were tempered in controlled atmosphere of hydrogen and water vapour (1.3 % H_2, 98.7 % H_2O) in the temperature range from 900 to 1300 °C for 3 h. The ratio of hydrogen and the water vapour was set in such a way, that the atmosphere of the heating would be in equilibrium to the magnetite and nickel as well. The requested equilibrium atmosphere of the heating is shown in Fig. 1. The p_{H_2}/p_{H_2O} equilibrial rations were calculated on the basis of thermodynamic data [5] for the respective redox reactions (Fig. 1). The diffusion couples were heated in a horizontal tubular furnace provided with silite heating elements. The furnace temperature was controlled by a chopper-bar regulator and measured by a Pt—PtRh 10 thermocouple. An automatic control system maintained specimen temperature within ±5 °C around the temperature set. The required heating atmosphere was adjusted by mixing the respective rates of flow of hydrogen and water vapour. A constant flow rate of water vapour was accomplished by controlled resistance heating of water in an Erlenmeyer flask placed in a vessel containing boiling water.

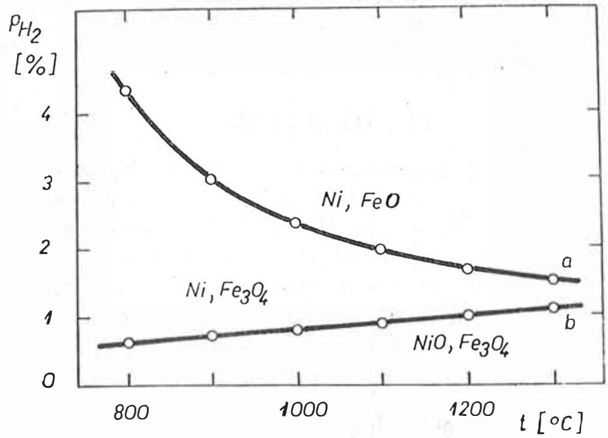

Fig. 1. Equilibrium hydrogen content in water vapour (vol. %) under total pressure of 1.013×10^5 Pa *for the reactions*

$$Fe_3O_4 + H_2 = 3\,FeO + H_2O \qquad (\textit{curve a}),$$
$$NiO + H_2 = Ni + H_2O \qquad (\textit{curve b}).$$

Following the heat treatment, the diffusion couples were sectioned perpendicularly to the interface with a diamond saw. The exposed surfaces were polished to optical quality with a 0.5 μm diamond abrasive. The whole procedure of the diffusion couples preparing (the original magnetite mineral plate, nickel-coated plate of the magnetite, the sample cut and polished after heating) is illustrated in Fig. 2.

An electron probe X-ray microanalyser JXA-5A (JEOL) was used to determine the concentration profiles by simultaneous counting of NiK_α and FeK_α X-rays. Each point of the concentration profile was obtained by integrating 10 s pulses for various step lenghts of sample shift (5, 10, 20 μm) in the direction perpendicular to the original diffusion boundary. The measuring of the concentration distribution was achieved step by step using the electric typewriter IBM and logical directing unit as well. This unit, as shown in Fig. 3, permitted automatic registration of the pulses' count in a closed cycle.

Pure components of the system were used as standards in quantitative point analysis. On the basis of the determined intensity values of characteristic X-ray radiation, that of the background and that of the standards it was possible to calculate the concentrations by weight of Ni and Fe on the CDC 3300 computer using the SONDA 03 program [6] which includes

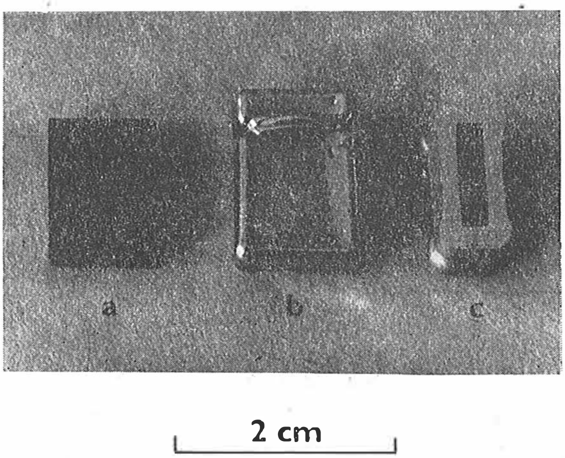

Fig. 2. Procedure for the preparation of diffusion couples; a — original sample of the Fe_3O_4 *mineral, b — nickel-coated plate of magnetite before heating, c — diffusion couple cut and polished after heating.*

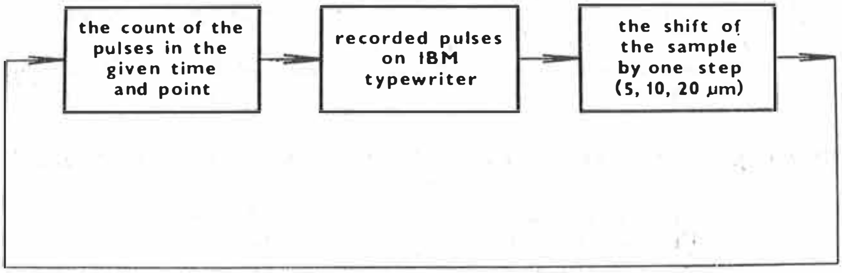

Fig. 3. Block diagram of the directing unit logic for automatic stepwise analysis.

corrections for absorption of X-radiation in the material of the specimen and in that of the standard, corrections for the effect of the atomic number and secondary fluorescence excitation respectively. For various temperatures, series of $C - x$ relationships, required for the calculation of the diffusion coefficients by the Matano-Boltzmann method, were thus obtained. The diffusion coefficients were calculated according to the following relationship

$$D_{C=C_1} = -\frac{1}{2t}\frac{\mathrm{d}x}{\mathrm{d}c}\int_0^{C_1} x\,\mathrm{d}c$$

using the CDC 3300 computer and program [7]. The experimental arrangement was chosen so (Fig. 2) as to meet the initial and the limiting conditions required by the Matano-Boltzmann method.

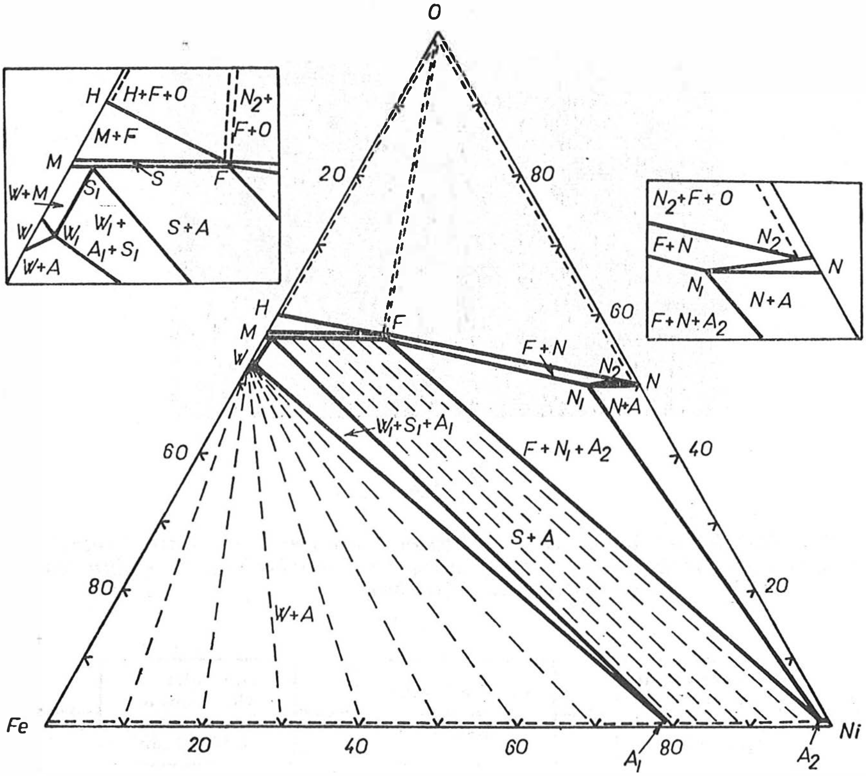

Fig. 5. Phase equilibria in the system Fe—Ni — O *at 1000 °C according to Dalvi and Smeltzer* [7];

W_1	$Ni_{0,01}Fe_{0,87}O$	(*wüstite*)
S_1	$Ni_{0,04}Fe_{2,96}O_4$	(*spinel*)
A_1	*79,6 at.* % Ni + *20,4 at.* % Fe	(*alloy*)
F	$NiFe_2O_4$	(*ferrite*)
N_1	$Fe_{0,13}Ni_{0,87}O$	(*nickel oxide*)
A_2	*99,5 at.* % Ni + *0,5 at.* % Fe	(*alloy*)
N_2	$Fe_xNi_{1-x}O$ $(x = 0,0005)$	(*nickel oxide*)
W	$Ni_xFe_{1-(x+x)}O$	(*wüstite*)
M	Fe_3O_4	(*magnetite*)
H	Fe_2O_3	(*hematite*)
N	$Fe_xNi_{1-x}O$	(*nickel oxide*).

DISCUSSION OF RESULTS

The qualitative character of the diffusion concentration profile of nickel at the boundary in the system Ni—Fe_3O_4 at temperatures from 900 to 1100 °C is illustrated in Fig. 4. The presence of a wüstite phase, which should have been formed at least in small amounts according to the phase diagram of the system Fe—Ni—O [8], [9], has not been observed. The phase diagram of the system Fe—Ni—O according to Dalvi and Smeltzer [8],

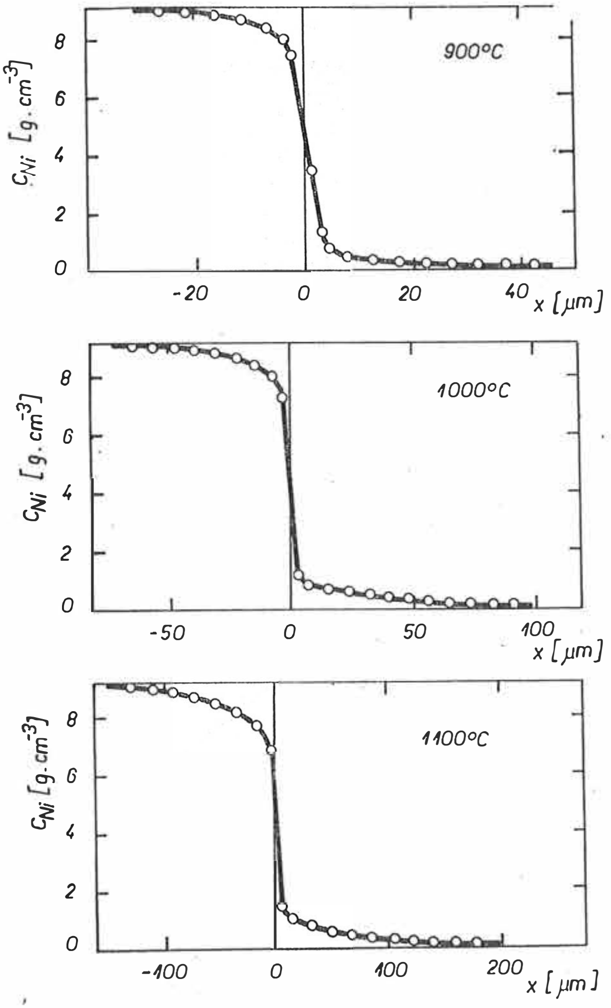

Fig. 6. Concentration profiles $C_{Ni} = f(x)$ *in the temperature range from 900 to 1100 °C, 3 h.*

which represents the most recent knowledge of the system, is shown in Fig. 5. The concentration profiles $C_{Ni} = f(x)$ determined for the individual temperatures are plotted in Fig. 6. The respective concentrations of nickel at the phase boundary, which represent the apparent solubility limits of Ni in Fe_3O_4 in the given experimental arrangement, as well as the determined values of diffusion coefficients including standard deviations of the measurements are listed in Table I. The diffusion coefficients $\tilde{D}^{Ni}_{Fe_3O_4}$ have been found to be concentration independent in the investigated range. The diffusion coefficients $\tilde{D}^{Ni}_{Fe_3O_4}$ characterizing interdiffusion in the system Ni—Fe_3O_4 are, within one order of magnitude, in a satisfactory agreement with the self-diffusion coefficients of Fe in Fe_3O_4 [1]—[3].

Table I

Apparent solubility limits for Ni in Fe_3O_4 and the determined values of diffusion coefficients $\tilde{D}^{Ni}_{Fe_3O_4}$

t [°C]	p_{O_2} [atm.]	$C^{Ni}_{Fe_3O_4}$ [wt. %]	$\tilde{D}^{Ni}_{Fe_3O_4}$ [cm^2s^{-1}]
900	2.5×10^{-13}	4.1 ± 0.5	$(1.4 \pm 0.6) \times 10^{-10}$
950	2.0×10^{-12}	4.6 ± 0.4	$(4.9 \pm 0.5) \times 10^{-10}$
1000	1.4×10^{-11}	5.3 ± 0.4	$(9.1 \pm 0.4) \times 10^{-10}$
1050	8.3×10^{-11}	5.7 ± 0.3	$(2.5 \pm 0.4) \times 10^{-9}$
1100	4.4×10^{-10}	6.5 ± 0.3	$(7.7 \pm 0.3) \times 10^{-9}$

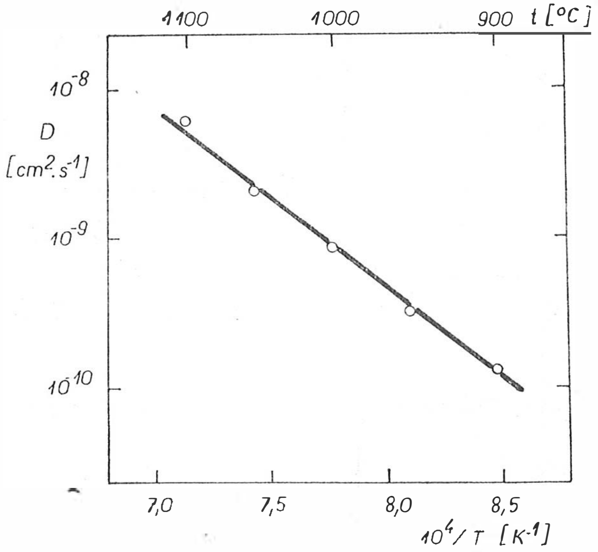

Fig. 7. Temperature dependence of the diffussion coefficient $\tilde{D}^{Ni}_{Fe_3O_4}$.

From the temperature dependence of the diffusion coefficient $\tilde{D}^{Ni}_{Fe_3O_4}$ (Fig. 7) in the 900 to 1100 °C temperature range the following relationship was found

$$\tilde{D}^{Ni}_{Fe_3O_4} = 42{,}7 \exp(-2.6 \times 10^2 \text{ kJ mol}^{-1}/RT).$$

For the purpose of comparison the diagram in Fig. 8 includes the temperature dependence of self-diffusion coefficients of Fe in Fe_3O_4 [1] and those of Ni in $Ni_xFe_{3-x}O_4$ for the ratio Fe/Ni = 3.5 [4]. The determined activation energy 2.6×10^2 kJ mol^{-1}, which in the system Ni—Fe_3O_4 characterizes interdiffusion of Ni and Fe cations by the mechanism of cationic vacancies, is approximately identical with the self-diffusion activation energy of Fe in Fe_3O_4 [2] and with that of Ni in $Ni_xFe_{3-x}O_4$ for the ratio Fe/Ni = 3.5 [4].

In the temperature range of 1150—1300 °C, formation of a three-phase reaction product consisting of spinel [$Ni_xFe_{3-x}O_4$], wüstite [(Ni, Fe)O] and metal [(Ni, Fe)] at the boundary Ni—Fe_3O_4 was observed. The phases present in the reaction product were identified by X-ray diffraction analysis as well as by electron probe X-ray microanalysis. The existence of the phases found is in qualitative agreement with the phase diagram of the system Fe—Ni—O [8] (Fig. 5) as well as with the phase diagram suggested by Tretyakov [9] on the basis of the data given in literature [10], [11]. The coexistence of three phases is also reported by Paladino [12] in his study of equilibria of the system Fe—Ni—O at various temperatures and partial pressures of oxygen.

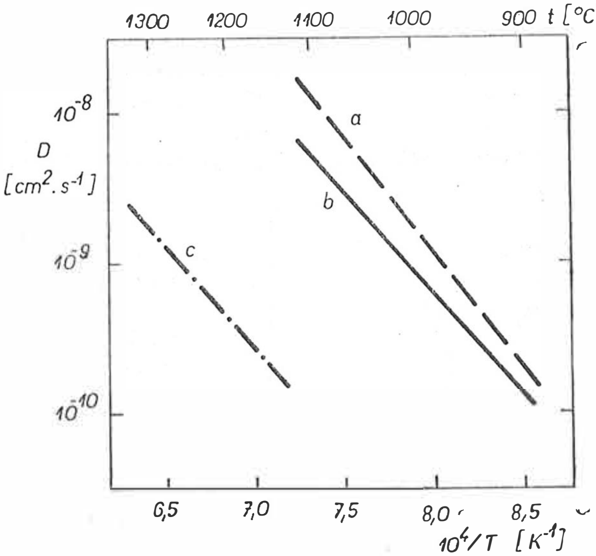

Fig. 8. Comparison of the temperature dependence of $\tilde{D}^{Ni}_{Fe_3O_4}$ *(curve b) with that of self-diffusion coefficients of* Fe *in* Fe_3O_4 *(curve a)* [1] *and of* Ni *in* $Ni_xFe_{3-x}O_4$ *for the* Fe/Ni *ratio = of 3.5 (curve)* [4].

Formation of the reaction product and the diffusion profile of nickel across the reaction layer at 1150 °C is illustrated by Fig. 9. The presence of spinel [$Ni_xFe_{3-x}O_4$], wüstite [(Ni, Fe)O] and precipitated metal [(Ni, Fe)] in the form of spherical particles is well observable in the detailed picture of the reaction layer (Fig. 10). The respective concentration profile $C_{Ni} = f(x)$ is plotted in Fig. 11. Quantitative analysis of the composition of each phase present carried out by electron probe X-ray microanalysis showed that with increasing temperature the nickel content of wüstite increases from 14 wt. % (at 1150 °C) up to 26 wt. % (at 1300 °C). These values are in a disagreement with those reported by Benard [13] according to whom the maximum solubility of NiO in wüstite does not exceed 10.4 wt. % and also differs markedly from the equilibrium content of Ni in wüstite (0.53 wt. %) as reported in the recent study [8]. The high values of Ni-concentration in the wüstite phase are evidently due to the fact that equilibrium conditions have not been reached. A decreasing nickel content in the spinel phase $Ni_xFe_{3-x}O_4$ was also observed with increasing temperature. The concentrations found of Ni in the spinel phase were: 18 wt. % at 1150 °C and 10 wt. % at 1300 °C.

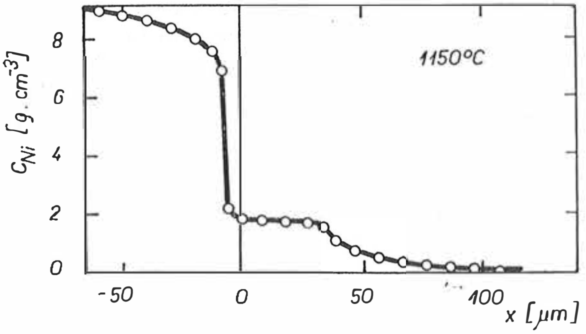

***Fig. 11.** Concentration profile* $C_{Ni} = f(x)$ *at 1150 °C, 3 h.*

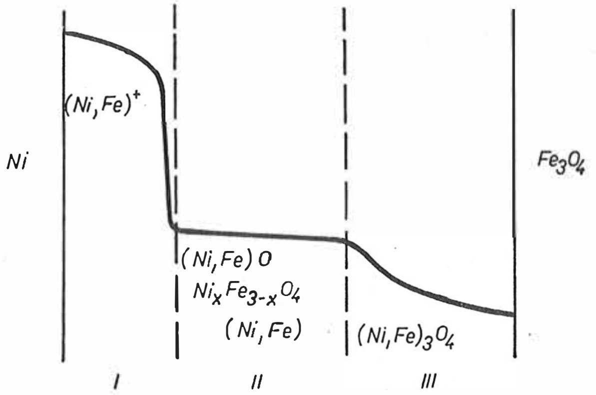

***Fig. 14.** Schematic diagram of the characteristic situation in the system* Ni — Fe_3O_4 *in the temperature range from 1150 to 1300 °C 3 h;*
I — region of solid solution of Fe in Ni [(Ni, Fe)$^+$],
II — region of solid solution of Ni *in wüstite* [(Ni, Fe) O],
— region of the spinel phase [$Ni_xFe_{3-x}O_4$],
— region of the metal phase [(Ni, Fe)],
III — region of solid solution of Ni *in magnetite* [$(Ni, Fe)_3O_4$].

The complex structure of the reaction layer at 1300 °C is illustrated by Fig. 12, as well as by the detailed X-ray and electron images respectively (Fig. 13), where the respective phases of the reaction product have been marked. The particles of the alloy phase are in the product layer present in two different shapes (Fig. 13, region "B"). Besides the primary precipitation product of the alloy [(Ni, Fe)] (spherical particles), there occurs during the cooling of the samples a secondary precipitation of needle-like crystals of the metal phase. The X-ray image of Ni K_α shows, that the concentration of nickel decreases in the surroundings of the alloy precipitates as a consequence of decomposition of the reaction product.

A schematic diagram of the characteristic situation in the system Ni—Fe_3O_4 after heat treatment of the diffusion couples in the temperature range from 1150 to 1300 °C is shown in Fig. 14. The first step in the formation of the reaction product probably comprises oxidation of Ni to NiO at the phase boundary Ni—Fe_3O_4.

CONCLUSION

The products of interdiffusion in the system Ni—Fe_3O_4 in the temperature range from 900 to 1300 °C under atmospheric pressure in controlled atmosphere of hydrogen and water vapour (1.3 % H_2, 98.7 % H_2O) have been investigated.

1. Coexistence of the metal phase and magnetite only was found in the temperature range from 900 to 1100 °C. Diffusion coefficients $\tilde{D}^{Ni}_{Fe_3O_4}$ characterizing interdiffusion in the system Ni—Fe_3O_4 were determined. The following relationship was found to hold in the 900 to 1100 °C temperature range

$$\tilde{D}^{Ni}_{Fe_3O_4} = 42.7 \exp(-2.6 \times 10^2 \text{ kJ mol}^{-1}/RT).$$

2. A reaction product consisting of the spinel, wüstite and a metal phase respectively was identified in the temperature range from 1150 to 1300 °C at the boundary in the system Ni—Fe_3O_4. This is in agreement with the phase equilibrium in the system Fe—Ni—O. The nickel content was found to increase with increasing temperature in the (Ni, Fe) O phase and to decrease in the $NiFe_2O_4$ phase. The determined solubility values of nickel in nickelwüstite are considerably higher than the equilibrium values published so far.

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ŠTÚDIUM VZÁJOMNEJ DIFÚZIE V SÚSTAVE Ni — Fe_3O_4

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V sústave Ni—Fe_3O_4 sa v oblasti teplôt 900—1300 °C študovala vzájomná difúzia niklu a železa a interakcia kovového niklu s magnetitom z hľadiska chemického a fázového zloženia produktov.

Sendvičové usporiadanie vzoriek bolo realizované galvanicky poniklovanými doštičkami prírodného minerálu Fe_3O_4 (obr. 2). Vzorky sa temperovali v kontrolovanej atmosfére vodík—vodná para (1,3 % H_2, 98,7 % H_2O) pri teplotách 900—1300 °C po dobu 3 h. Meranie sa vykonalo na elektrónovom mikroanalyzátore JXA-5A (Jeol). Difúzne koeficienty sa vypočítali pomocou Matano—Boltzmannovej metódy.

V oblasti teplôt 900—1100 °C sa pozorovala len koexistencia kovovej fázy a magnetitu (obr. 4). V študovanej teplotnej oblasti sa stanovili difúzne koeficienty $\tilde{D}^{Ni}_{Fe_3O_4}$, ktoré charakterizujú vzájomnú difúziu v sústave Ni—Fe_3O_4. V meraných medziach koncentrácií niklu sa zistila koncentračná nezávislosť difúzneho koeficienta. Z teplotnej závislosti $\tilde{D}^{Ni}_{Fe_3O_4}$ (obr. 7) sa vypočítala aktivačná energia difúzie rovná 2,6 . 10^2 kJ mol^{-1}.

V oblasti teplôt 1150—1300 °C sa na rozhraní v sústave Ni—Fe_3O_4 identifikoval reakčný produkt tvorený fázami spinelu [$NiFe_2O_4$], wüstitu [(Ni, Fe) O] a kovovou fázou [(Ni, Fe)] (obr. 9, 10, 12, 13). So stúpajúcou teplotou sa zistil rast obsahu Ni vo fáze (Ni, Fe) O a pokles obsahu Ni vo fáze $NiFe_2O_4$. Stanovené hodnoty rozpustnosti niklu vo wüstite pritom podstatne prevyšujú doposiaľ publikované rovnovážne hodnoty.

Obr. 1. *Rovnovážny obsah vodíka vo vodnej pare (obj. %) pri celkovom tlaku 1,013 . 10^5 Pa pre reakcie*

$$Fe_3O_4 + H_2 = 3\,FeO + H_2O \qquad (\textit{krivka } a),$$
$$NiO + H_2 = Ni + H_2O \qquad (\textit{krivka } b).$$

Obr. 2. *Postup prípravy sendvičového usporiadania vzoriek; a — pôvodná vzorka minerálu* Fe_3O_4, *b — galvanicky poniklovaná vzorka pred temperovaním, c — nábrus kolmého rezu vzorky po temperovaní.*

Obr. 3. *Bloková schéma logickej riadiacej jednotky.*

Obr. 4. *Vzájomná difúzia v sústave* Ni—Fe_3O_4 *pri teplotách 900 °C (a), 1000 °C (b), 1100 °C (c) a čase difúzie 3 h; elektrónové obrázky chemického zloženia; röntgenové obrázky plošnej distribúcie niklu s čiarovým koncentračným profilom* Ni K_α.

Obr. 5. *Fázové rovnováhy v sústave* Fe—Ni—O *pri teplote 1000 °C podľa Dalviho a Smeltzera* [7];

W_1	$Ni_{0,01}Fe_{0,87}O$	(*wüstit*)
S_1	$Ni_{0,04}Fe_{2,96}O_4$	(*spinel*)
A_1	*79,6 at.* % Ni + *20,4 at.* % Fe	(*zliatina*)
F	$NiFe_2O_4$	(*ferit*)
N_1	$Fe_{0,13}Ni_{0,86}O$	(*nikeloxid*)
A_2	*99,5 at.* % Ni + *0,5 at.* % Fe	(*zliatina*)
N_2	$Fe_xNi_{1-x}O$ ($x = 0,0005$)	(*nikeloxid*)
W	$Ni_xFe_{1-(x+y)}O$	(*wüstit*)

M	Fe_3O_4	(*magnetit*)
H	Fe_2O_3	(*hematit*)
N	$Fe_xNi_{1-x}O$	(*nikeloxid*).

Obr. 6. Priebeh závislosti $C_{Ni} = f(x)$ *v oblasti teplôt 900—1100 °C a čase difúzie 3h.*

Obr. 7. Teplotná závislosť, difúzneho koeficienta $\tilde{D}^{Ni}_{Fe_3O_4}$.

Obr. 8. Porovnanie teplotnej závislosti $\tilde{D}^{Ni}_{Fe_3O_4}$ *(krivka b) s teplotnými závislosťami samodifúznych koeficientov* Fe *v* Fe_3O_4 *(krivka a) [1] a* Ni *v* $Ni_xFe_{3-x}O_4$ *pre pomer Fe/Ni = 3,5 (krivka c) [4].*

Obr. 9. Vzájomná difúzia v sústave Ni—Fe_3O_4 *pri teplote 1150 °C a čase difúzie 3h, elektrónový obrázok chemického zloženia, röntgenový obrázok plošnej distribúcie atómov niklu s čiarovým koncentračným profilom* NiK_α.

Obr. 10. Detailný obrázok reakčnej vrstvy pri teplote 1150 °C; elektrónový obrázok chemického zloženia, röntgenový obrázok plošnej distribúcie atómov niklu.

Obr. 11. Priebeh závisloti $C_{Ni} = f(x)$ *pri teplot*$_\mathrm{o}$ *1150 °C a čase difúzie 3 h.*

Obr. 12. Časť reakčnej vrstvy pri teplote 1300 °C; elektrónový obrázok chemického zloženia.

Obr. 13. Detailný obrázok časti reakčnej vrstvy pri teplote 1300 °C; elektrónové obrázky chemického zloženia, röntgenové obrázky plošnej distribúcie atómov niklu.

Obr. 14. Schéma celkovej situácie v sústave Ni—Fe_3O_4 v oblasti teplôt *1150—1300* °C;
I — oblasť tuhého roztoku Fe *v* Ni [(Ni, Fe)$^+$],
II — oblasť tuhého roztoku Ni *vo wüstite* [(Ni, Fe) O],
— oblasť spinelovej fázy [$NiFe_2O_4$],
— oblasť kovovej fázy [Ni, Fe)],
III — oblasť tuhého roztoku Ni *v magnetite* [$(Ni, Fe)_3O_4$].

ИССЛЕДОВАНИЕ ВЗАИМОДИФФУЗИИ В СИСТЕМЕ Ni—Fe_3O_4

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Кафедра химической технологии силикатов химико-технологического факультета Словацкого политехнического института, Братислава

В системе Ni—Fe_3O_4 в области температур 900—1300 °С исследовали взаимодиффузию никеля и железа и взаимодействие металлического никеля с магнетитом с точки зрения химического и фазового состава продуктов.

Подвергаемые исследованию образцы состояли из гальванически никелированных пластинок природного минерала Fe_3O_4 (рис. 2). Образцы темперировали в контролируемой среде водород — водяной пар (1,3 % H_2, 98,7 % H_2O) при температурах 900—1300 °С во время 3 часов. Измерение проводили с помощью электронного микрозонда JXA-5A (Jeol). Коэффициенты диффузии расчитывали методом Матано—Болцманна.

В области темперетур 900—1100 °С заметили только сосуществование металлической фазы с магнетитом (рис. 4). В исследуемой температурной области установили коэффициенты диффузии $\tilde{D}^{Ni}_{Fe_3O_4}$, характеризующие взаимодиффузию в системе Ni—Fe_3O_4. В измеряемых пределах концентраций никеля установили концентрационную независимость коэффициента диффузии. На основании зависимости $\tilde{D}^{Ni}_{Fe_3O_4}$ (рис. 7) расчитали энергию активации диффузии, составляющую 2,6 . 10^2 кJ мол$^{-1}$.

В области температур 1150—1300 °С на разделе в системе Ni—Fe_3O_4 идентифицировали продукт реакции, образовавшийся фазами шпинели [$Ni_xFe_{3-x}O_4$], вюстита [(Ni,Fe)O] и металической фазой [(Ni, Fe)] (рис. 9, 10, 12, 13). С растущей температурой установили рост содержания никеля во фазе (Ni, Fe)O и понижение содержания никеля во фазе $Ni_xFe_{3-x}O_4$. Установленные величины растворимости никеля в вюстите существенно выше по сравнению с до сих пор опубликованными величинами равновесия.

Рис. 1. Равновесное содержание водорода в водяном паре (% *по объему*) *при общем давлении 1,013 . 10^5 Pa для реакций*

$$Fe_3O_4 + H_2 = 3\,FeO + H_2O \qquad \textit{(кривая а)},$$
$$NiO + H_2 = Ni + H_2O \qquad \textit{(кривая б)}.$$

Рис. 2. Способ приготовления образца типа сендвич;
а — исходный образец минерала Fe_3O_4, *b — гальванически никелированный образец до темперирования, с — аншлиф перпендикулярного сечения образцом после темперирования.*

Рис. 3. Блок-схема логической управляющей единицы.

Рис. 4. Взаимодиффузия в системе Ni—Fe_3O_4 *при температурах 900 °С* (*а*), *1000 °С* (*b*), *1100 °С* (*с*) *и времени диффузии 3 часа; электронные фотосъемки химическоо состава, рентгеновские фотосъемки, распределения атомов никеля с линейным профилем концентрации* NiK_α.

Рис. 5. Фазовые равновесия в системе Fe—Ni—O *при температуре 1000 °С согласно Дальви и Шмелцеру* [7]

M_1	$Ni_{0,01}Fe_{0,87}O$	(*вюстит*)
S_1	$Ni_{0,04}Fe_{2,96}O_4$	(*шпинель*)
A_1	*79,6 ат.* % Ni + *20,4 ат.* % Fe	(*сплав*)
F	$NiFe_2O_4$	(*ферит*)
N_1	$Fe_{0,13}Ni_{0,87}O$	(*никелоксид*)
A_2	*99,5 ат.* % Ni + *0,5 ат.* % Fe	(*сплав*)
N_2	$Fe_xNi_{1-x}O$ ($x = 0,0005$)	(*никелоксид*)
W	$Ni_xFe_{1-(x+y)}O$	(*вюстит*)
M	Fe_3O_4	(*магнетит*)
H	Fe_2O_3	(*гематит*)
N	$Fe_xNi_{1-x}O$	(*никелоксид*)

Рис. 6. Ход зависимости $C_{Ni} = f(x)$ *в области температур 900—1100 °С и времени 3 часа.*

Рис. 7. Температурная зависимость коэффициента диффузии $\tilde{D}^{Ni}_{Fe3O4}$.

Рис. 8. Сопоставление температурной зависимости $\tilde{D}^{Ni}_{Fe3O4}$.
(*кривая b*) *с температурными зависимостями коэффициентов самодиффузии* Fe *в* Fe_3O_4 (*кривая а*) [*1*] *и* Ni *в* $Ni_xFe_{3-x}O_4$ *для отношения* Fe/Ni = *3,5* (*кривая с*) [*4*].

Рис. 9. Взаимодиффузия в системе Ni—Fe_3O_4 *при температуре 1150 °С и времени диффузии 3 часа; электронная фотосъемка химического состава,*
рентгеновская фотосъемка распределения атомов никеля с линейным профилем концентрации NiK_α.

Рис. 10. Деталь реакционного слоя при температуре 1150 °С; электронная фотосъемка химическово состава;
рентгеновская фотосъемка,
распределения атомов никеля.

Рис. 11. Ход зависимости $C_{Ni} = f(x)$ *при температуре 1150 °С и времени диффузии 3 часа.*

Рис. 12. Часть реакционного слоя при температуре 1300 °С; электронная фотосъемка химического состава.

Рис. 13. Деталь части реакционного слоя при температуре 1300 °С; электронные фотосъемки химического состава,
рентгеновские фотосъемки распределения атомов никеля.

Рис. 14. Схема общего положения в системе Ni—Fe_3O_4 *в области температур 1150—1300 °С;*
I — область твердого раствора Fe *в* Ni [(Ni, Fe)$^+$],
II — область твердого раствора Ni *в вюстите* [(Ni, Fe)O], *область шпинельной фазы* [$Ni_xFe_{3-x}O_4$], *область металлической фазы* [(Ni, Fe)],
III — область твердого раствора Ni *в магнетите* [$(Ni, Fe)_3O_4$].

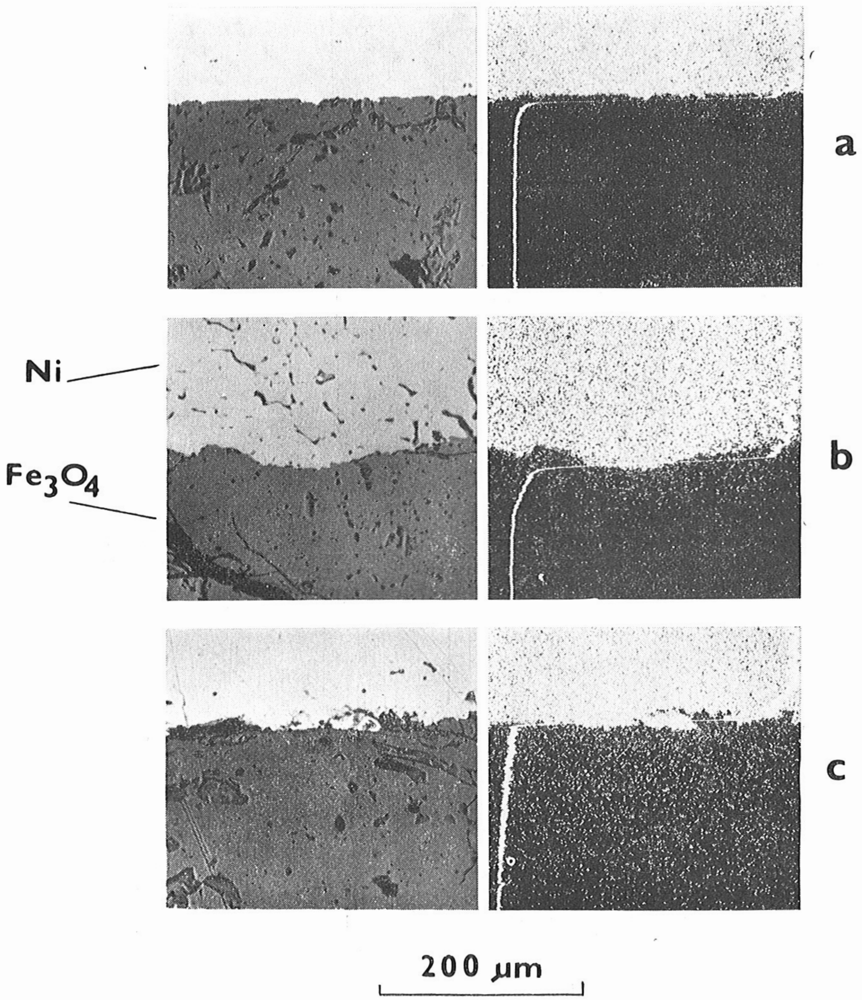

Fig. 4. Interdiffusion in the system Ni — Fe$_3$O$_4$ *at 900 °C (a), 1000 °C (b), 1100 °C (c), after* 3 h *of diffusion;*
electron images of chemical composition, X-ray images of NiK$_\alpha$ *with line scan profile of* Ni.

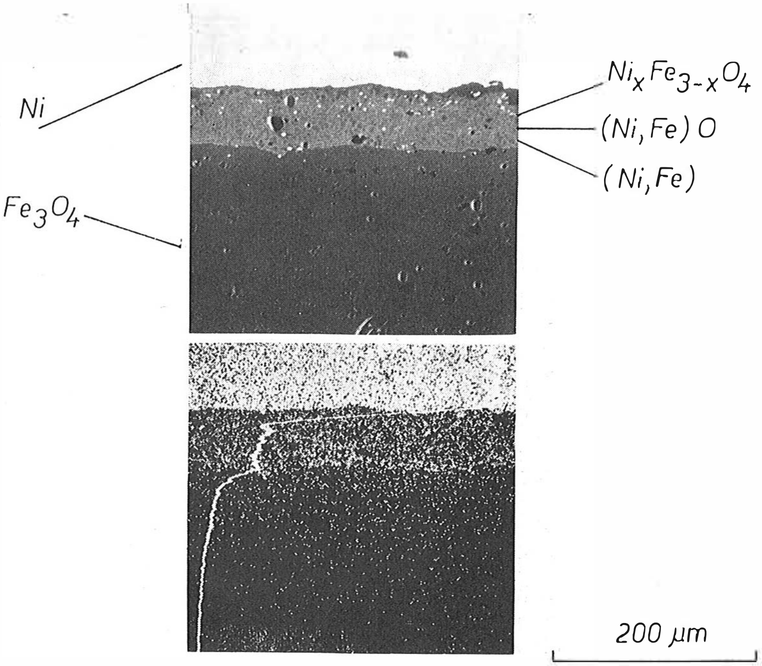

Fig. 9. Interdiffusion in the system Ni — Fe_3O_4 *at 1150 °C after 3 h of diffusion; electron image of chemical composition, X-ray image of* NiK_α *with line scan profile of* Ni.

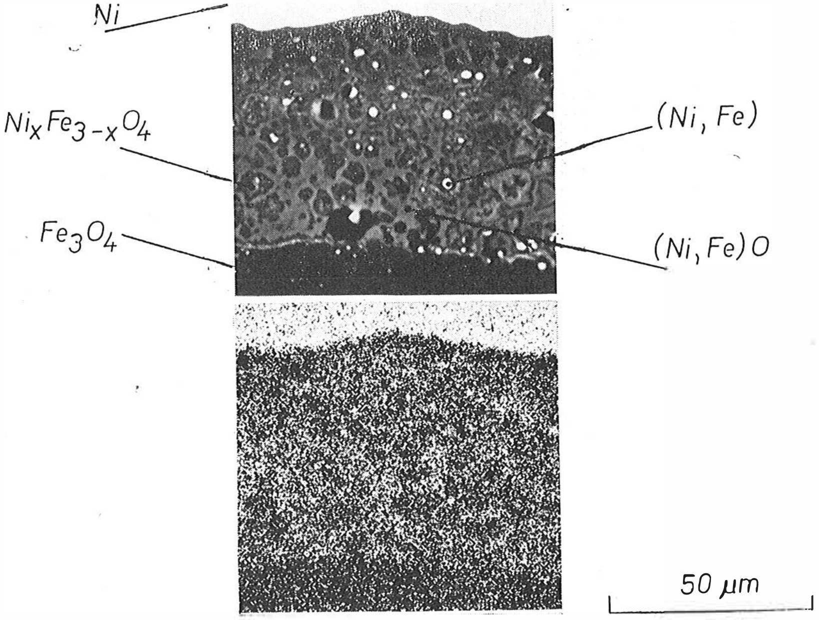

Fig. 10. A typical detailed cross-sectional view of the reaction product layer at 1150 °C, 3 h; electron image of chemical composition, X-ray image of NiK_α

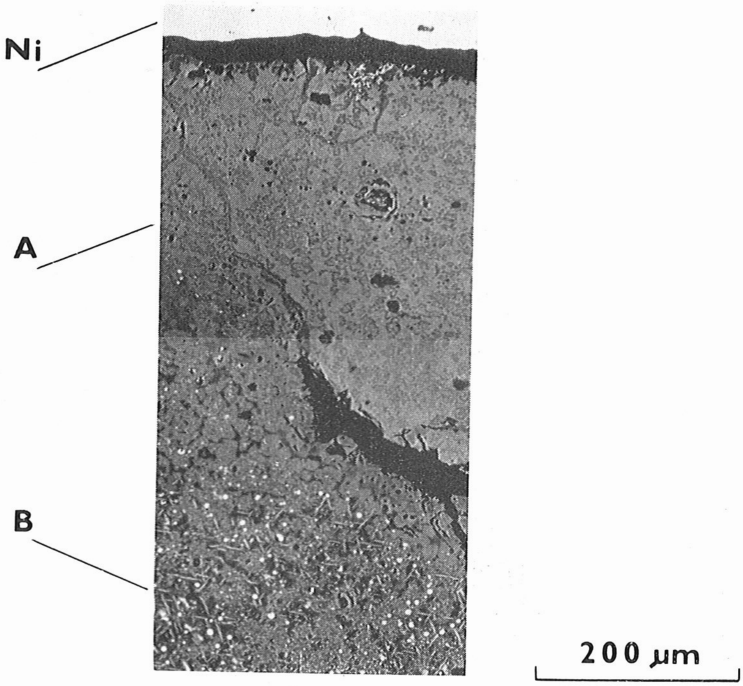

Fig. 12. A typical cross-sectional view of the reaction product layer at 1300 °C, *3 h; electron image of chemical composition.*

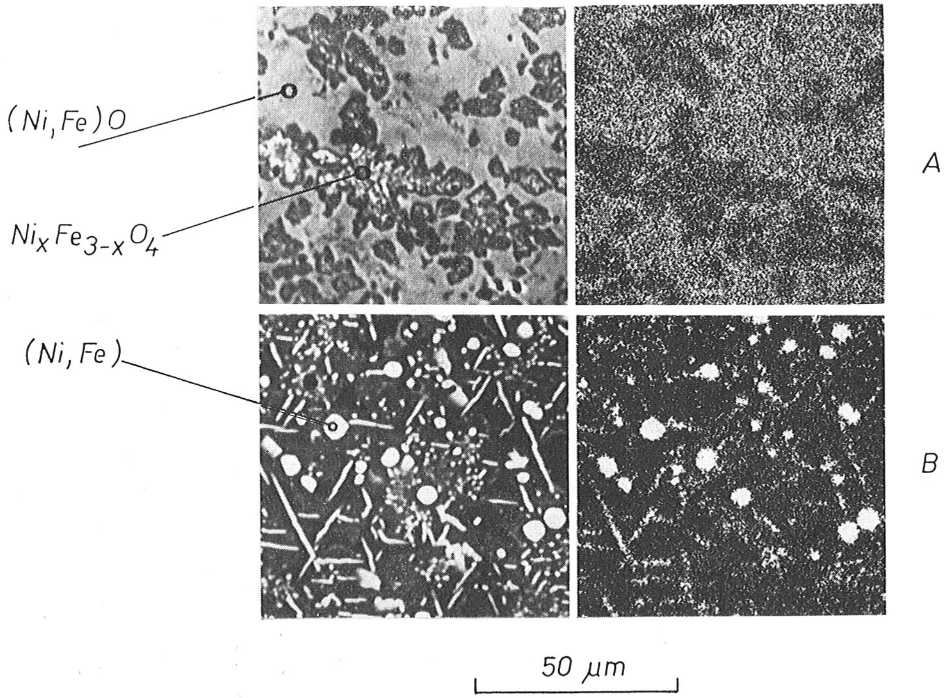

Fig. 13. Detailed picture of the reaction product layer at 1300 °C, *3 h; electron images of chemical composition, X-ray images of* NiK_{α}.