

Simultaneous measurement of Cr, Mn and Fe diffusion in chromium-manganese steels*

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Abstract The paper presents an application of multitracer method to diffusion measurement in Cr-Mn steels. Radioisotope tracers of chromium ^{51}Cr , manganese ^{54}Mn and iron ^{59}Fe were used simultaneously in the diffusion process. Measurements of gamma-ray spectra and the proper analysis enabled evaluation of concentration distribution for each tracer. As a new tool, artificial neural networks (ANN) method was used for analysis of spectra. The proper solution of the diffusion model was applied to the experimental tracers' distribution data and diffusion coefficients were determined.

Key words radiotracer • diffusion • steel • spectrum • artificial neural networks

Introduction

Selection of the metallic materials used in modern industrial technologies is determined by the conditions in which they are supposed to work. They are often exposed to aggressive atmospheres and high temperatures. Industrial steels, which show high heat-resistance, are composed mainly on the base of iron, chromium and nickel. At present the chromium-manganese steels are the objects of interest due to their lower price and better heat-resistance as well as mechanic properties. The full description of the mechanism of Cr-Mn steels oxidation requires the knowledge of each partial process. For example, it should be considered: transport of steel components in the metallic phase, outward diffusion of steel components through the scale and inward diffusion of oxidant through the scale. The transport of metals in the metallic phase is supposed to be the slowest partial process, determining the rate of the whole steel oxidation.

The aim of this paper is the examination of self-diffusion processes in austenitic Cr-Mn steels in order to evaluate diffusion coefficients of chromium, manganese and iron. The serial sectioning technique was used to evaluate diffusion coefficient of radioisotopes of chromium ^{51}Cr , manganese ^{54}Mn and iron ^{59}Fe . This technique involved electrolytic dissolution of a metallic sample on a filter paper soaked in electrolyte. In experimental procedure, the activity distribution on a filter paper as well as the residual activity of the specimen were calculated from gamma-spectra acquired

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Table 1. Chemical composition of the Cr-Mn steels

Grate of steel	Concentration of elements (% wt.)				
	C	Cr	Mn	Si	Ca
5H17G17 (Cr17Mn17)	0.52	17.40	16.89	–	–
3H13G18S2Ca (Cr13Mn18SiCa)	0.32	12.84	18.82	1.80	0.95

by a scintillation (NaI(Tl)) counter. Due to small peak resolution and a significant contribution of the Compton component in the spectra, the features characteristic for different tracers are not easily recognizable and the ANN's were used in their analysis. Diffusion coefficients have been evaluated by applying the solution of the diffusion model (II Fick's law) for a boundary as thin layer geometry and a semi-infinite solid.

Experimental

Two types of austenitic steels, having the NaCl crystal structure (cubic face centred structure) were used in the experiment. Their composition is given in Table 1. The steels samples of 14 mm diameter and 1 mm thick were carefully polished and degreased with acetone.

One surface of each sample was coated with a very thin layer of radioactive atoms by the electrolytic reduction of chromium, manganese and iron from the radioactive solutions of the chlorides: $^{51}\text{CrCl}_3$, $^{54}\text{MnCl}_2$ and $^{59}\text{FeCl}_3$ (Fig. 1a). The diffusion experiment was performed by annealing the prepared samples within evacuated and sealed quartz ampoules at a temperature of 1173 K. The duration of diffusional annealing was chosen in such a way that the thickness of the sample was greater than the penetration depth of the tracer [1, 6]. This allows considering the discussed system in terms of approximation to a semi-infinite solid. The penetration profiles were determined by the serial sectioning method [5]. This technique involved electrolytic dissolution of a metallic sample on a filter paper soaked in electrolyte (25% vol. conc. H_2SO_4 , 25% vol. conc. H_3PO_4 , 50% vol. $\text{C}_2\text{H}_6\text{O}_2$). The apparatus used in this procedure is shown in Fig. 1b. The thickness of each removed section (about 3 μm) was determined by

gravimetric and direct measurement. The mass of the sample was measured using an analytical balance with the accuracy 10^{-4} g.

In experimental, procedure the gamma-spectra of the removed layer were measured using the scintillation (NaI(Tl)) spectrometer combined with a multichannel analyzer (500 channels). The examples of the gamma-spectra (after background subtraction) for different layers are shown in Fig. 2. For deep layers, the activities of the tracers were significantly decreased. For the analysis of spectra, artificial neural network was applied.

Analysis of spectra

The main aim of the ANN application in the presented case was evaluation of the activity of chromium ^{51}Cr , manganese ^{54}Mn , and iron ^{59}Fe from gamma-spectra (Fig. 2). In this case, the input data vector $\mathbf{X}(x_1, x_2, \dots, x_{500})$ included the count numbers for each spectrum channel and the output vector $\mathbf{Y}(y_1, y_2, y_3)$ included the relative activities of the three isotopes. For the network training process, the proper set of input (\mathbf{X}) and output (target) data (\mathbf{Y}) had been prepared. Some part of the data had been used for network learning and the other part for testing. Dozens of network structures had been tested for the optimal ANN to choose. Finally, it turned out that the one-layer linear network is optimal for the presented aim. This network executes the following relation:

$$(1) \quad \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} = \begin{bmatrix} w_{1,1} & w_{1,2} & \dots & w_{1,500} \\ w_{2,1} & w_{2,2} & \dots & w_{2,500} \\ w_{3,1} & w_{3,2} & \dots & w_{3,500} \end{bmatrix} \times \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_{500} \end{bmatrix}$$

or in matrix notation:

$$(2) \quad \mathbf{Y} = \mathbf{W} \times \mathbf{X}$$

where: \mathbf{W} is the [3, 500] dimensions matrix which represents the one-layer linear network with 3 neurons and 500 inputs for each neuron.

The relation (1) is calculated in the following way:

$$(3) \quad y_j = \sum_{i=1}^{500} w_{ji} \cdot x_i.$$

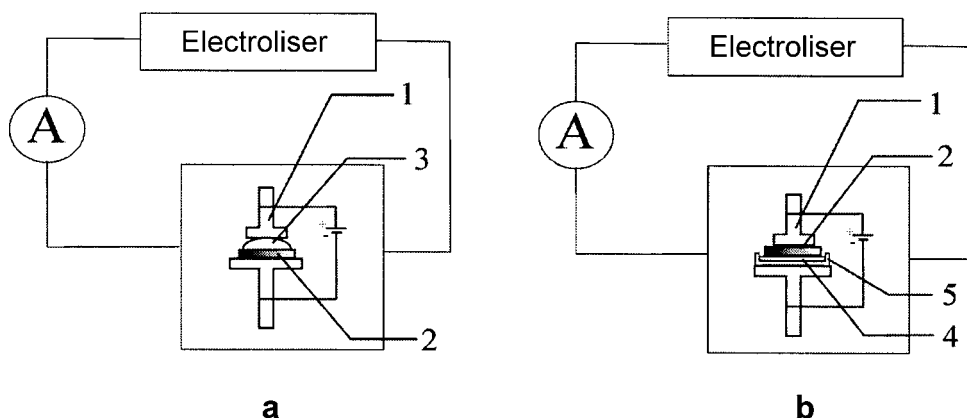


Fig. 1. Apparatus used for: a – electrolytic deposition of radioactive layers on the sample surface; b – anodic dissolution of thin metal layers from the sample surface. 1 – anode; 2 – sample; 3 – radioactive solution of chlorides; 4 – filter paper; 5 – aluminium vessel.

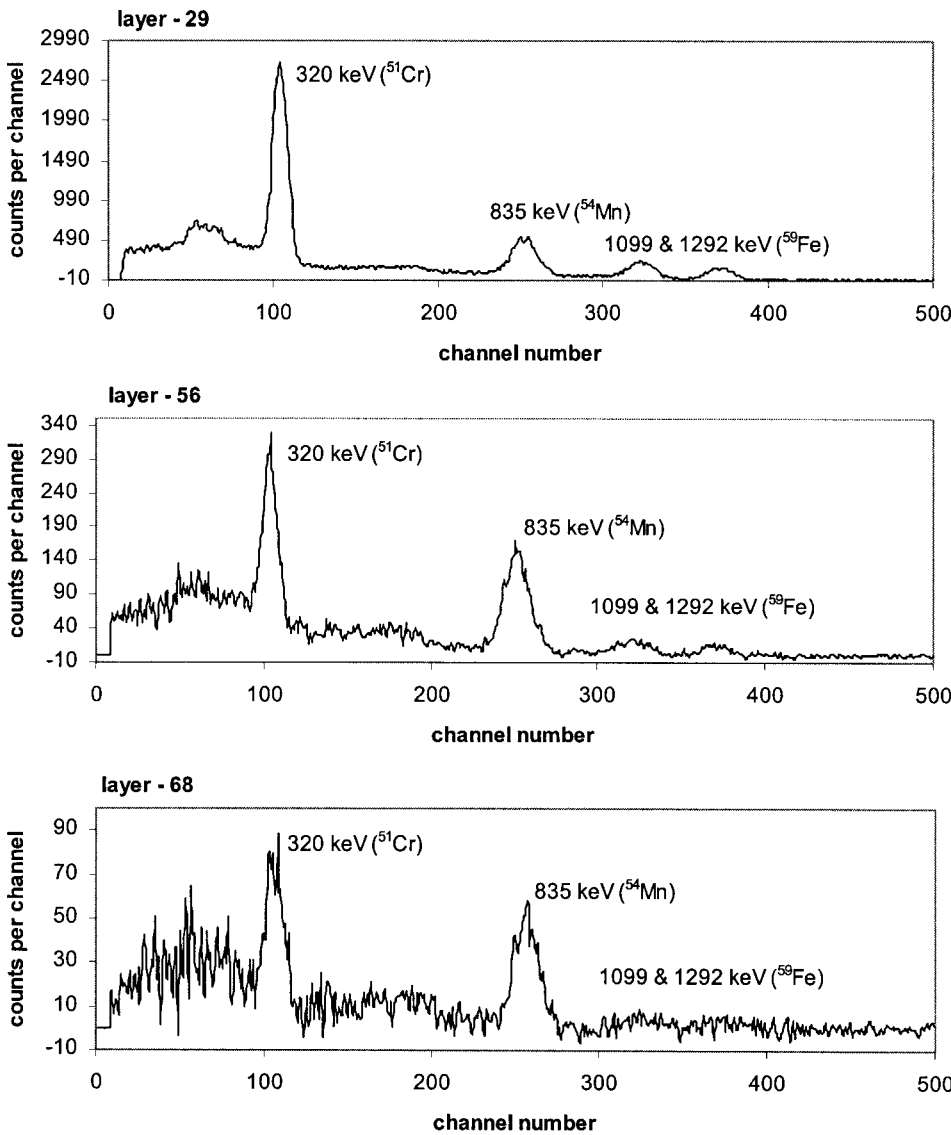


Fig. 2. Examples of the gamma-spectra for different layers.

The element values of matrix \mathbf{W} should be arranged in such a way that the first row evaluates the activity of chromium ^{51}Cr (y_1) from the spectrum (\mathbf{X}), the second and the third evaluates the activity of manganese ^{54}Mn (y_2) and iron ^{59}Fe (y_3), respectively. Least squares criterion and the gradient iteration method have been used for matrix (\mathbf{W}) element values calculation [7]. For verification of this method, a Ge spectrometer has been used in order to precisely analyze gamma-ray spectra of the selected samples (layers). A comparison of the results from the Ge spectrometer measurement and from the scintillation spectrometer supported by the ANN method is shown in Fig. 3. Both results show a full conformity to statistical error limits.

Tracers concentration analysis and results

The ANN method allowed evaluation of total activity for each tracer and each sample layer as a function of layer depth. The total activities were re-calculated to the specific activities $A_s(x)$ according to the following formula:

$$(4) \quad A_s(x) = \frac{A_T(x)}{\Delta m}$$

where: x – sample layer depth from the metal surface; $A_T(x)$ – total activity of tracer in the sample layer; Δm – decrease of sample mass after removing the layer.

In this method, the specific activity $A_s(x)$ is proportional to the tracer concentration $c(x)$. At presented experiment, the boundary conditions were a semi-infinite solid (metal) and a thin layer of the tracers on metal surface at the diffusion process beginning. The solution of II Fick's law for tracer concentration distribution is described by the Eq. (5) where also proportionality between $c(x)$ and $A_s(x)$ is shown.

$$(5) \quad A_s(x) \approx c(x) = c_0 \cdot \exp\left(\frac{-x^2}{4D_T t}\right)$$

where: t – time of the diffusion process; D_T – diffusion coefficient of the radioactive tracer; c_0 – tracer concentration for $x = 0$.

The normalized concentration function can be presented in the following form:

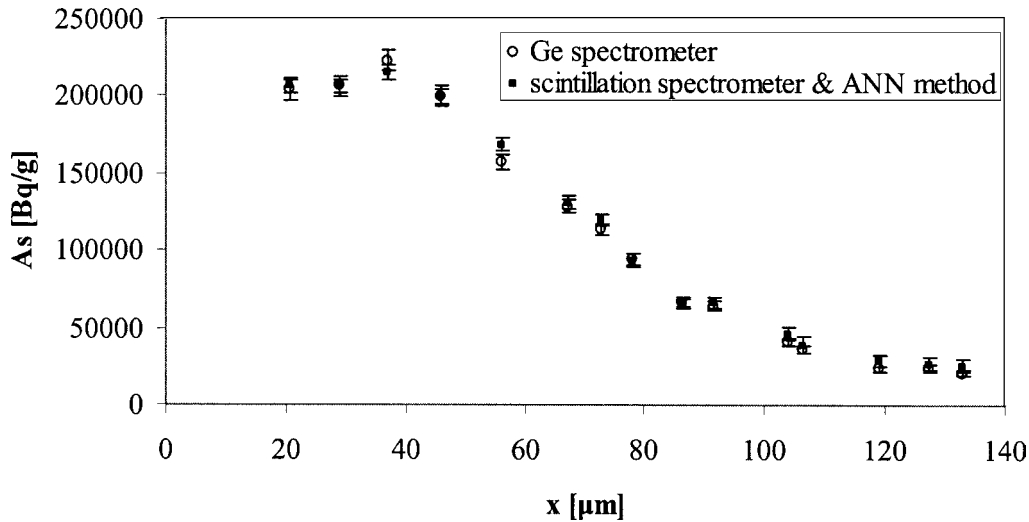


Fig. 3. Results from the Ge spectrometer and from the scintillation spectrometer supported by ANN method.

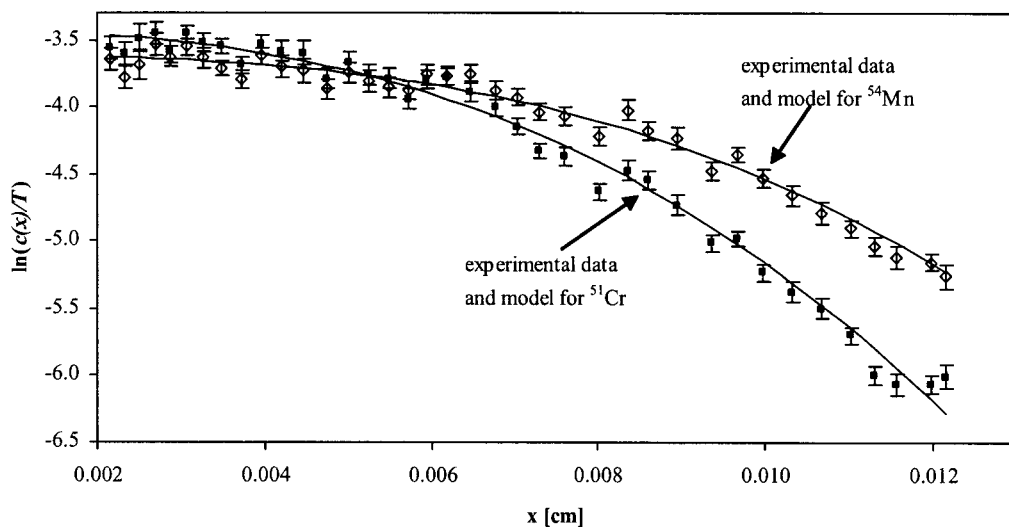


Fig. 4. Experimental data and the models fitted for a 3H13G18S2Ca steel.

$$(6) \quad \ln[c(x)/c_0] = -\frac{1}{4D_T t} \cdot x^2.$$

$$(7) \quad D = \frac{D_T}{f}$$

The above functions are fitted to the experimental data using the software package MATLAB 6.5. The results of fitting are shown in the Fig. 4. Poor adjustment of the analytical curve is noticeable in the case of measurements of initially removed layers. Considering the fact that points under discussion cover the thickness of about 20 μm , the adjustment was carried out for the subsequent points. The explanation of the primary point behaviour is rather difficult. Poor adhesion of the isotopic layer as well as the deformation of the sample surface might be the main source of this error.

The diffusion coefficient of atoms – D , is related to the one of radiotracer – D_T , by the following formula:

where: f – correlation factor. It is influenced by the crystal structure and the mechanism of diffusion. For the cubic, face centered crystal structure its value is equal to 0.78146 [3]. The values of the self-diffusion coefficients of metals are listed in Table 2.

Discussion

The diffusion rates of chromium and iron are comparable and lower than that of manganese. The diffusion rate of metals is higher in the 3H13G18S2Ca steel, containing Si and Ca. The faster transport of manganese partly explains the morphological structure of the scale

Table 2. Diffusion coefficients of metals in the studied Cr-Mn steels

Metal	D_{Cr} ($\text{cm}^2 \cdot \text{s}^{-1}$)	D_{Mn} ($\text{cm}^2 \cdot \text{s}^{-1}$)	D_{Fe} ($\text{cm}^2 \cdot \text{s}^{-1}$)
5H17G17	$(8.11 \pm 0.36) \times 10^{-12}$	$(12.78 \pm 0.69) \times 10^{-12}$	$(7.77 \pm 0.45) \times 10^{-12}$
3H13G18S2Ca	$(11.08 \pm 0.84) \times 10^{-12}$	$(19.32 \pm 1.92) \times 10^{-12}$	$(11.03 \pm 0.96) \times 10^{-12}$

that is mainly built of the manganese compounds. Moreover, the depletion of manganese close to the metal/scale interface causes phase transformation from austenitic to ferritic structure and causes a decrease of the diffusion rate [2]. As it was mentioned above, the dominant components of the scales formed on Cr-Mn steels in SO₂ are MnO and the MnCr₂O₄ spinel. The diffusion coefficients of Cr, Mn and Fe in the MnCr₂O₄ spinel were not found. However, the diffusion coefficient of Mn in MnO is about 10⁻⁹ cm²·s⁻¹ at 1173 K [4], higher than that in steel. Hence, it is possible that the transport in the metal phase is the slowest partial process determining the corrosion rate.

Conclusions

- The ANN method for multitracer experiment has been developed and applied.
- The lattice diffusion is the dominant mechanism of metals' transport.
- The diffusion rates of Fe and Cr are comparable and lower than the diffusion rate of Mn.
- The diffusion rate of metals is higher in the 3H13G18S2Ca steel, containing Si and Ca.
- Faster depletion of Mn in the near metal/scale region causes phase transformation from austenitic

to ferritic structure. In consequence, the oxidation rate of the steels decreases.

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