Chemical and Electrochemical Isolation of AlN and MnS Precipitates from Fe—3 % Si Steels

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The aim of the presented paper is the analysis of the chemical composition of the precipitates in Fe—3 % Si steels with the emphasis on AlN and MnS particles. It is shown that the ratio between the Al and Mn contents in extracted particles depends on the chemical composition of the matrix (total amount of Al, N, and S). The results are compared using the electron microscopy analysis.

The nonmetallic microphases (precipitates) represent negligible amount in the composition of the steels but they are significant for their properties. The content of the nitrogen, sulfur, carbon, and oxygen, the amount of the elements which represent the specimens, the thermo-deformation schedule of the treatment are fundamental factors which determine the production of the nonmetallic microphases.

AlN and MnS particles are utilized in Fe—3 % Si steels as inhibitors of the secondary recrystallization process with the aim to prefer the development of the Goss orientation grains [1]. The retardation effect depends on their total volume fraction and dispersion. The dispersion parameters depend beside the chemical composition also on the history of preceding treatment of material, especially at the hot rolling stage. The atmosphere composition in the course of the recrystallization annealing also influences the particle system [2].

For the correct determination of the precipitation parameters various methods are used, but up-to-now we do not have the universal one. The simultaneous use of chemical and electron microscopy analyses seems to be optimal.

In silicon steels, in dependence on their chemical composition and the heat treatment, other nitride phases may exist, *e.g.* SiN, (Al, Si, Mn)N, (Si, Mn)N$_2$, Si$_2$N$_3$, α- and β-Si$_3$N$_4$, SiON,.. However, their direct influence on the grain boundary movement is negligible with regard to theirs. On the other hand, they exhaust the respective elements necessary for the formation of fine effective particles.

The aim of the presented paper is the chemical and electron microscopy analysis of the composition of the precipitates in Fe—3 % Si steels with the emphasis on AlN and MnS particles.

EXPERIMENTAL

In majority of cases the state of precipitation is determined indirectly by measurement of some physical and mechanical properties. Direct methods (chemical analysis and transmission electron microscopy) have some advantages and disadvantages. The development of the methodology of the isolation and analysis of microphases was performed on the specimens of silicon steels with the chemical composition presented in Table 1 (in mass %). Sawdust as well as two types of cylinders ($l = 10$ mm, $r = 3$ mm and $l = 45$ mm, $r = 5$ mm) of as-hot rolled strips were used.
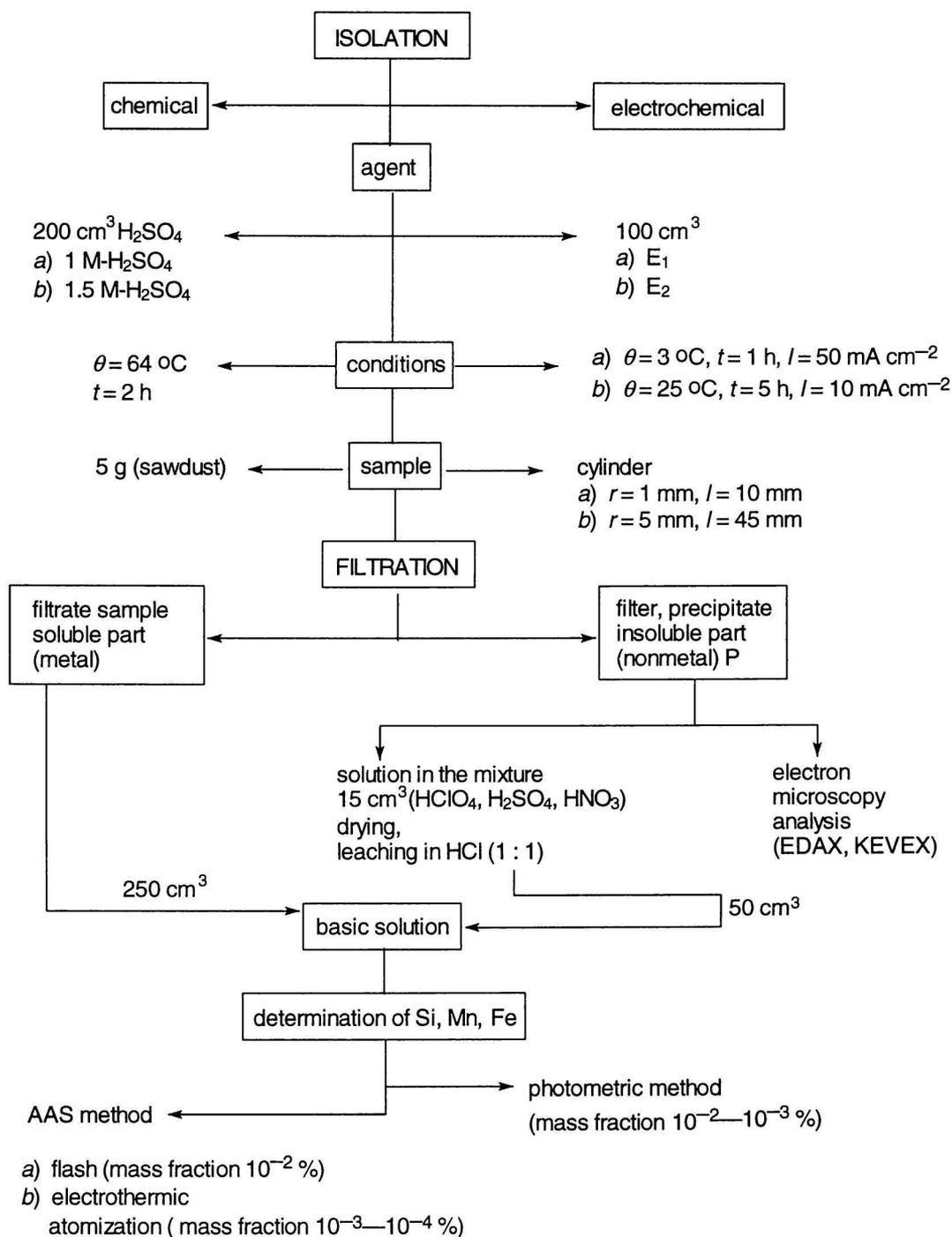
The following isolation methods were tested on individual specimens:

– dissolution in diluted acids (sawdust) [3, 4];
– electrochemical isolation (cylinders) [5—7].

Both methods are described in Scheme 1, where two variants are shown, namely at the chemical isola-

Table 1. Chemical Composition of the Steels (w/%)

Specimen	C	Mn	Si	P	S	Al	Cu	Ni	Cr	As	N
42901	0.05	0.15	2.90	0.008	0.011	0.036	0.012	0.009	0.013	0.009	0.011
33	0.03	0.19	3.29		0.006	0.006	–	–	–	–	0.007
34	0.03	0.19	3.32	–	0.006	0.007	–	–	–		0.007

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                          ┌──────────────┐
                          │  ISOLATION   │
                          └──────┬───────┘
         ┌──────────┐           │          ┌──────────────────┐
         │ chemical │ ◄─────────┴────────► │ electrochemical  │
         └──────────┘                      └──────────────────┘
                          ┌─────────┐
                          │  agent  │
                          └────┬────┘
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200 cm³ H₂SO₄ ◄──────────────┴──────────────► 100 cm³
a) 1 M-H₂SO₄   *a*) E₁
b) 1.5 M-H₂SO₄   *b*) E₂

$\theta = 64\ ^{o}C$ ◄──── │ conditions │ ────► *a*) $\theta = 3\ ^{o}C$, $t = 1$ h, $I = 50$ mA cm⁻²
$t = 2$ h   *b*) $\theta = 25\ ^{o}C$, $t = 5$ h, $I = 10$ mA cm⁻²

5 g (sawdust) ◄──── │ sample │ ────► cylinder
                                     a) $r = 1$ mm, $l = 10$ mm
                                     b) $r = 5$ mm, $l = 45$ mm

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                       ┌──────────────┐
                       │  FILTRATION  │
                       └──────┬───────┘
   ┌──────────────────┐       │        ┌──────────────────────┐
   │ filtrate sample  │ ◄─────┴──────► │ filter, precipitate  │
   │ soluble part     │                │ insoluble part       │
   │ (metal)          │                │ (nonmetal) P         │
   └────────┬─────────┘                └──────────┬───────────┘
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solution in the mixture   electron
15 cm³ (HClO₄, H₂SO₄, HNO₃)   microscopy
drying,   analysis
leaching in HCl (1 : 1)   (EDAX, KEVEX)

250 cm³ ──────────► ┌────────────────┐ ◄────── 50 cm³
                     │ basic solution │
                     └───────┬────────┘

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              ┌──────────────────────────┐
              │ determination of Si, Mn, Fe │
              └──────────────┬───────────┘
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                                        ──────► photometric method
                                                (mass fraction 10⁻²—10⁻³ %)

AAS method ◄──────

a) flash (mass fraction 10^{-2} %)
b) electrothermic
    atomization (mass fraction 10^{-3}—10^{-4} %)

Scheme 1
The procedure of the isolation of AlN and MnS.

tion (CHI) 200 cm³ of agent was used, in variant *a*) 1 M-H₂SO₄ and in variant *b*) 1.5 M-H₂SO₄. (For the chemical method a critical value t_{crit} of the time of isolation is typical [8]. Before or after this one we do not have a full sample of the precipitates – for $t \leq t_{crit}$ not full sample of precipitates has been solved and for $t \geq t_{crit}$ some unstable parts of the precipitates are

also solved. Therefore in order to take into account the dependence of the chemical isolation on the t_{crit} we used two various agents.)

At the electrochemical isolation (EI) the electrolytes with the composition *a*) 100 cm³ E₁: 20 % NaCl, 6 % trisodium acetate, and 2 % citric acid, H₂O (pH = 4.1), and in case of *b*) variant 500 cm³ E₂:

Table 2. Isolation in 1 M-H_2SO_4 (*a*) and 1.5 M-H_2SO_4 (*b*)

Specimen variant	42901			33			34		
	a	*b*	E_2	*a*	*b*	E_1	*a*	*b*	E_1
$w(P)/\%$	0.060	0.160	0.621	0.162	0.092	0.350	0.290	0.150	0.420
$w_s(Al)/\%$	0.030	0.029		0.0015	0.0028	–	0.002	0.002	
$w_i(Al)/\%$	0.006	0.007	0.0017	0.0064	0.0045	0.005	0.0066	0.0029	0007
$w_s(Si)/\%$	2.42	2.88		3.06			3.07		
$w_i(Si)/\%$	0.0085	0.005	0.010		0.010	0.010		0.010	0.010
$w(MnS)/\%$	0.150	0.150		0.190	0.190		0.19	0.19	
$w_i(Mn)/\%$	0	0	0.0112	0	0	0.0066	0	0	0.010
$w_i(Fe)/\%$	0.0075	0.025	0.382	0.009	–	0.20	0.007		0.25
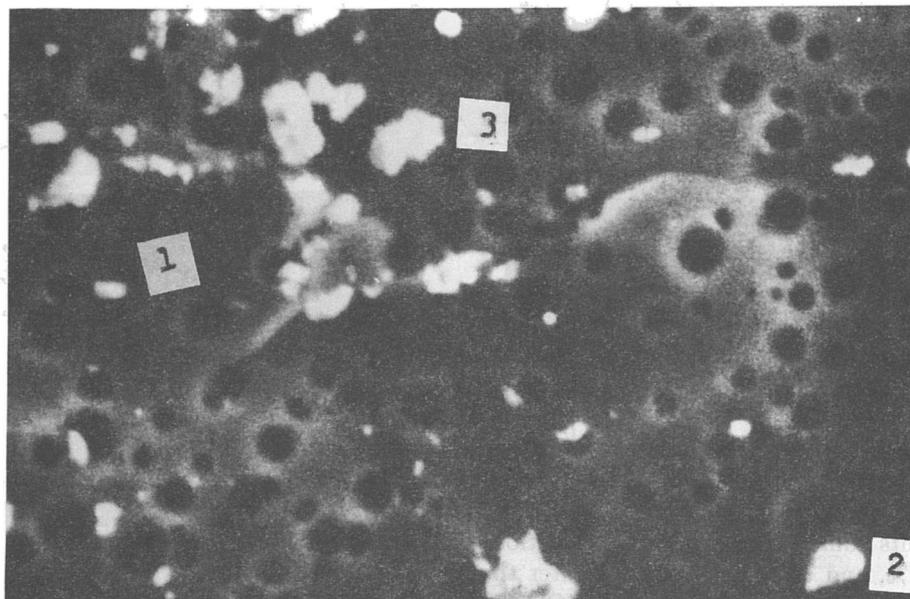
Fig. 1. SEM (EDAX) analysis of the precipitates from the sample 42901 (chemical isolation in 1.5 M-H_2SO_4).

5 % sodium citrate, 1.2 % KBr, 0.5 % ascorbic acid, H_2O (pH = 5.6—5.8) were used (we used two various electrochemical liquid agents for the sake to obtain MnS (with the fixed values of the electric current I, time t, and temperature θ), which is not possible to isolate as an unsolved part by the chemical isolation). At the chemical separation of the particles 5 g of sawdust were dissolved in H_2SO_4 in a temperature-controlled oven under constant conditions. At the second method the cylinder was anodically dissolved in the electrolyte. The cathode was formed by Pt gauze.

After completion of both separation methods (chemical and electrochemical), the insoluble part (precipitates) was separated from the soluble part by filtering using a SYMPOR filter (0.23 μm) [8, 9]. The precipitates were subjected to electron microscopy and microchemical analyses after drying and weighing.

The chemical analysis of the extracted particles was performed according to Scheme 1. In basic solutions, namely of precipitates (50 cm^3) and in soluble part (250 cm^3) the element contents were determined by the atomic absorption spectroscopy (AAS) and spectrophotometric methods. The AAS method was performed using an atomic absorption spectrometer (Zeiss, Jena), model 30, equipped with the corrector of the background of discharge tube with a hollow cathode. The photometric method was performed using a spectrometer Hitachi U-1100. All the used chemicals were anal. grade. The extracted precipitates were analyzed by electron microscopy using SEM in combination with EDAX or KEVEX microanalyzers.

RESULTS AND DISCUSSION

The individual isolations of precipitates (chemical and electrochemical) were carried out from Fe—3 % Si steels on the same specimens several times for the sake of comparison of SEM and microchemical analyses. After isolation of the specimens two parts were obtained by filtering: a soluble part and an insoluble
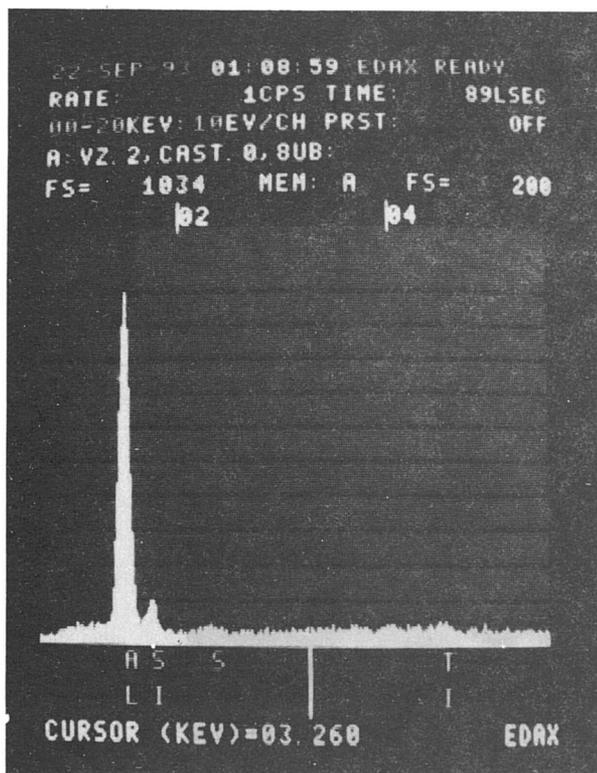
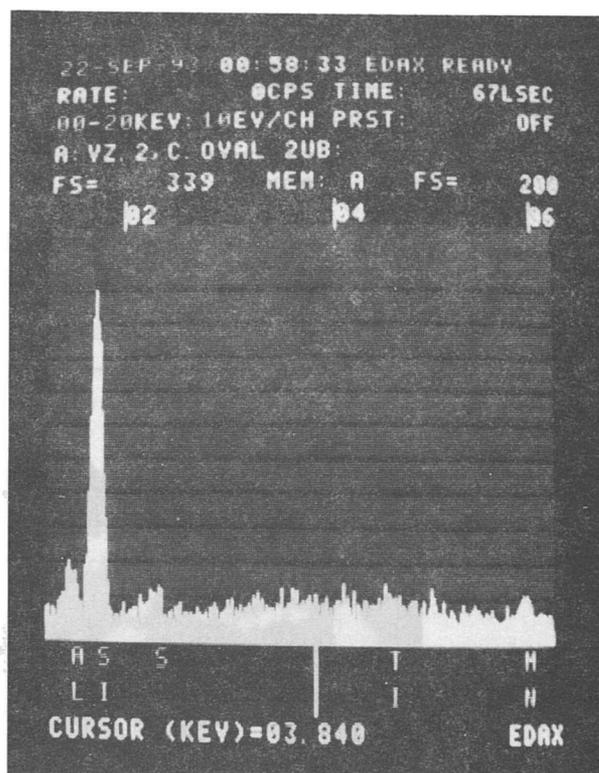**Fig. 2.** Spectrum of the particle clusters No. 1 (1.5 M-H_2SO_4).

Fig. 3. Spectrum of the particle clusters No. 2 (1.5 M-H_2SO_4).

(precipitates) one in a black powder form, which remained finally dispersed on the filter in a very small amount (0.5—2.0 mg).

Table 2 presents numerical values of mass fractions $w(P)/\%$, $w_s(X)/\%$, and $w_i(X)/\%$, obtained after the CHI of the specimens in 1 M- and 1.5 M-H_2SO_4 and after the EI (using also two various agents – E_1 and E_2). $w(P)$ is the mass fraction of precipitates in the steel specimen, $w_s(X)$ the mass fraction of X element in the soluble part of the steel specimen, and $w_i(X)$ the mass fraction of X element in the insoluble part of the steel specimen. The results presented in the tables are the mean values of the several points with the errors less than the last number for each value.

By comparison of both isolation types using chemical analysis Mn was determined only at the electrochemical separation in the insoluble part of the steel specimens. SEM analysis of the precipitates obtained by both extraction methods was performed on the specimen 42901. Fig. 1 of SEM (EDAX) analysis shows individual particles or their clusters. Figs. 2—4 present the respective spectra of the above-mentioned particles – it is probably the AlN particle and the particle clusters with Si_3N_4 and Fe_3C contents after the chemical isolation in 1.5 M-H_2SO_4. Fig. 5 shows the precipitate cluster after the EI in E_2. Fig. 6 presents the respective spectrum of that precipitate cluster recorded by the SEM (KEVEX) method and beside are the measured values of the concentrations of individual elements. The precipitates from the specimen
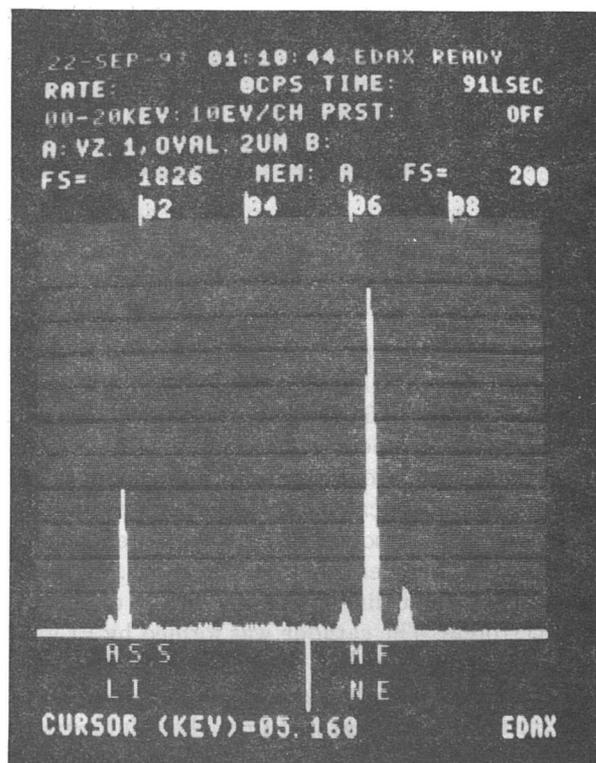

Fig. 4. Spectrum of the particle clusters No. 3 (1.5 M-H_2SO_4).

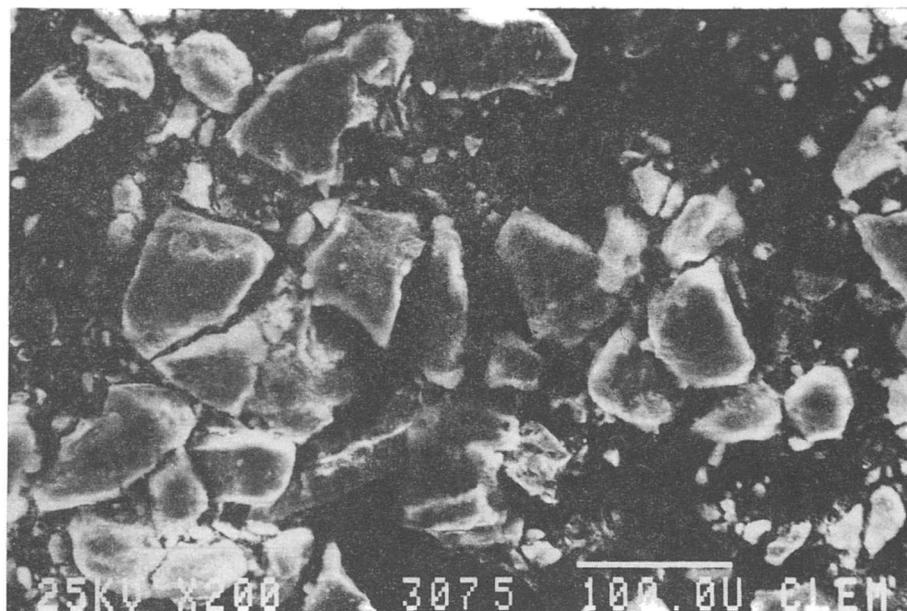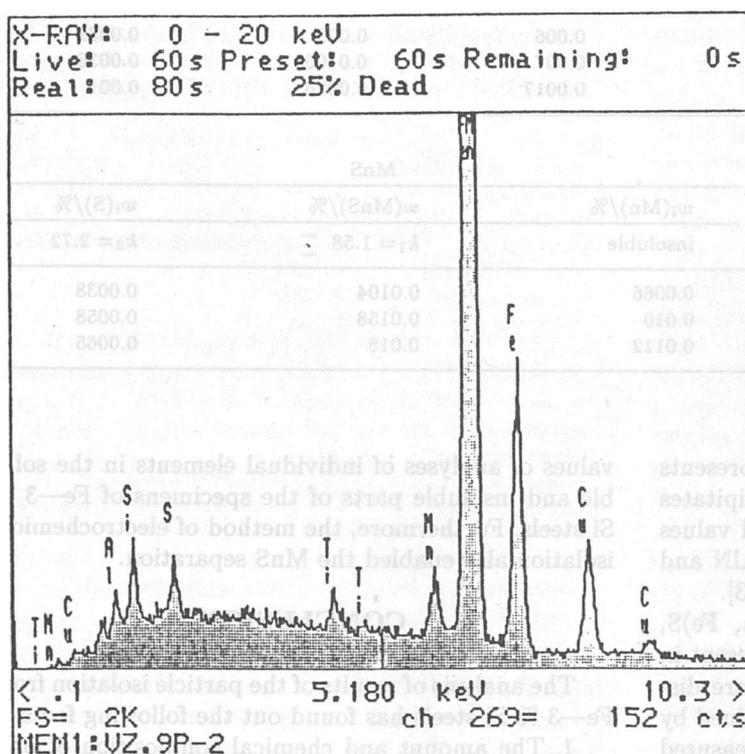42901 after three successive extractions in E_2 were also subjected to chemical analysis. Table 3 presents the

Fig. 5. SEM analysis of the precipitates from the sample 42901 (electrochemical isolation in E_2).

ELMT	APP	mass fraction
FeK	2	64.361
FeL	2	59.270
CuK	2	5.69
CuL	2	2.188
MnK	2	1.643
TiK	2	0.625
SK	0	0.989
SiK	2	0.808
AlK	2	0.337
[3 ZAF'S]		

Fig. 6. Global spectrum of the clusters of the precipitates from the sample 42901 (electrochemical isolation in E_2 by the SEM (KEVEX) method).

mass fractions of elements in the insoluble part of the specimen $w_i(X)$ measured by the AAS method and the mass fraction $w_p(X)$ of X element in the precipitate obtained by the SEM method shown in Fig. 6.

It follows from the comparison of chemical and SEM analyses from Table 3 that at the same isolation procedure the abundance of the elements in the insoluble part of the specimen $(w_i(X))$ is approximately the same, and hence in the precipitate $(w_p(X))$ – consider the fact that the values Mn and S in the precipitates (practically MnS) from the SEM analysis are approximately the same as the calculated sulfur from the mea-

Table 3. Chemical and SEM Analyses of the Elements in the Precipitates (E_2, Sample 42901)

Analysis $w(P)/\%$	Chemical analysis (AAS) 0.621		SEM (KEVEX) 0.646	
Element	$w_i(\text{meas},X)/\%$	$w_p(\text{calc},X)/\%$	$w_p(\text{meas},X)/\%$	$w_i(\text{calc},X)/\%$
Fe	0.382	61.19	64.34	0.415
Mn	0.0112	1.80	1.64	0.010
Al	0.0017	0.27	0.337	0.0021
Si	0.010	1.61	0.808	0.005
S	–	1.045	0.989	0.0063
Ti	–	–	0.625	0.004

Table 4. Chemical Composition of the Particles MnS and AlN

Specimen	Isolation	$w(P)/\%$	AlN		
			$w_i(\text{Al})/\%$	$w(\text{AlN})/\%$	$w_i(\text{N})/\%$
			insoluble	$k_1 = 1.52$	$k_2 = 2.92$
33	a	0.162	0.0064	0.0097	0.0033
	b	0.092	0.0045	0.0068	0.0023
	E_1	0.350	0.005	0.0076	0.0026
34	a	0.290	0.0066	0.010	0.0034
	b	0.150	0.0029	0.0044	0.0015
	E_1	0.420	0.007	0.0106	0.0036
42901	a	0.060	0.006	0.009	0.0031
	b	0.160	0.007	0.0106	0.0036
	E_2	0.621	0.0017	0.0026	0.001

Specimen	Isolation	MnS		
		$w_i(\text{Mn})/\%$	$w(\text{MnS})/\%$	$w_i(\text{S})/\%$
		insoluble	$k_1 = 1.58$	$k_2 = 2.72$
33	E_1	0.0066	0.0104	0.0038
34	E_1	0.010	0.0158	0.0058
42901	E_2	0.0112	0.018	0.0065

sured value Mn by the AAS [7, 10]. Table 4 presents the chemical composition of AlN and MnS precipitates from the specimen 42901. From the measured values of $w_i(\text{Mn})$ and $w_i(\text{Al})$ the mass fractions of AlN and MnS are obtained using k_1 and k_2 constants [3].

Other particles as α- and β-Si$_3$N$_4$, (Mn, Fe)S, SiO$_2$, Al$_2$O$_3$, MnO$_2$, Fe$_3$C, Fe$_2$O$_3$ are also present in the precipitates. The elements N, S, and O are distributed among these. In the precipitates obtained by isolation in E_2 from the specimen 42901 the measured values $w(X)$ of C, N, and O were: $w_p(\text{C}) = 12.50\ \%$, $w_p(\text{N}) = 2.29\ \%$, and $w_p(\text{O}) = 11.74\ \%$ and the values calculated from them $w_i(\text{C}) = 0.02\ \%$, $w_i(\text{N}) = 0.0066\ \%$, and $w_i(\text{O}) = 0.008\ \%$. The comparison of the measured value $w_p(\text{N})$ with the total sum of the nitrides nitrogen (Table 4) shows also a good agreement [7, 11].

Both the used methods of the particle separation enabled the isolation of nitride phases (AlN, Si$_3$N$_4$), or SiO$_2$, Fe$_3$C and the materialization of the obtained values of analyses of individual elements in the soluble and insoluble parts of the specimens of Fe—3 % Si steels. Furthermore, the method of electrochemical isolation also enabled the MnS separation.

CONCLUSION

The analysis of results of the particle isolation from Fe—3 % Si steels has found out the following facts:

1. The amount and chemical composition of precipitates is dependent on the separation method. A greater fraction of precipitates was obtained by electrochemical isolation, which is evidenced by the $w_i(\text{Mn})$ value, hence the presence of MnS phase, and a greater value of $w_i(\text{Fe})$, hence the presence of (Mn, Fe)S and Fe$_3$C.

2. A smaller fraction of precipitates was obtained by chemical isolation, but the value of $w_i(\text{Al})$, hence the content of AlN nitride phase, is greater than in the case of electrochemical separation. $w_i(\text{Si})$ is ap-

proximately the same, which is due to the chemical stability of α- and β-Si_3N_4, or SiO_2.

3. It follows from the comparison of chemical and SEM analyses that at the same isolation procedure the abundance of elements in the insoluble part of the specimen $(w_i(X))$, and hence in the precipitate $(w_p(X))$, is approximately the same.

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