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Identification of precipitations in anodically dissolved high-strength microalloyed Weldox steels

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ABSTRACT

Purpose: The aim of the investigations is to elaborate the optimum conditions of anodic dissolutions from high-strength microalloyed Weldox steels in order to obtain indispensable quantities of electrolytic extractions and to identify them by X-ray phase analysis.

Design/methodology/approach: Anodic dissolution of steel was carried out according to the potentiostatic method. In the X-ray qualitative analysis the comparative method was applied. The corrosion resistance of steels was determined by means of the first method of Stern - Tafel.

Findings: The activity of anodic dissolution of the investigated steel was determined in various solutions of electrolytes with different pH and a different complexive affect versus iron.

Practical implications: It has been found that the application of an optimal reagent for the anodic dissolution of Weldox Steel and of the chronopotentriometric method permit to get the required mass of electrolytic extraction for the qualitative X-ray phase analysis. Electrochemical investigations permitted also to assess preliminarily the corrosion resistance of the investigated steels.

Originality/value: It has been found that there exists a distinct relation between the mass of electrolytic extractions and the kind of the dissolved precipitation and the value of the electrochemical potential of the anodic dissolution of steel, which affects essentially the result of the X-ray phase analysis. Besides, a high corrosion resistance of the investigated steels to the destructive effect of a saline environment and a low resistance to an acid environment have been detected.

Keywords: Metallic alloy; Microalloyed constructional steels; Anodic dissolution; X-ray phase analysis; Corrosion resistance

PROPERTIES

1. Introduction

The tractability of microalloyed constructional steels for the production of high-strength products with a low transition temperature, good technological deformability and good weldability at reasonable costs decides about its general application to various structures of heavy machines, transport facilities, bridges, containers, etc [1-3].

Constructional microalloyed steels contain up to about 0.2 wt.% carbon and to about 1.8 wt.% manganese as well as microadditions of Nb, Ti and V in amounts up to 0.1 wt.%, sometimes a somewhat higher concentration of nitrogen and up to

0.005 wt.% boron, increasing the hardenability of the steel. An addition of up to 0.5 wt.% copper results in an increased atmospheric corrosion resistance of these steels. Weldox steels belong to high-strength welded low-alloy steels (type HSLA) [4-6].

Considerable mechanical properties of metallurgical products are obtained thanks to the fine-grained structure of recrystallized austenite due to the share of dispersive particles of interstitial phases of the type MX (M-Nb, Ti, V; X-N, C) precipitated in the γ-phase in the correctly chosen range of the temperature of hot-plastic treatment [7-9].

Besides the high mechanical properties of constructional microalloyed steels, their corrosion resistance is essential for their exploitation. A preliminary assessment of the corrosion resistance of the material in given corrosion conditions is possible by electrochemical investigations, which permit to gather in a short time data concerning the usability of the investigated materials for application in any given environment and also to assess several corrosive phenomena occurring on the surface of the materials and alloys as well as in protective coatings [10-13].

The aim of the investigations was to select and optimize the chemical composition of electrolytes and to determine their activity in the process of anodic dissolution of the investigated steels, as well as to determine the effect of the process conditions on the phase identification of Weldox 900 and Weldox 1300 steels by means of the X-ray diffraction. A complementary aim of the investigations was to assess the corrosion resistance of steel to the effect of saline and acid environments.

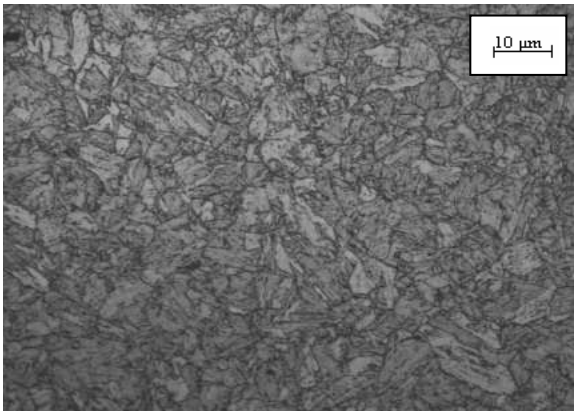
2. Experimental procedure

Investigations were carried out on high-resistant microalloyed constructional Weldox steels, resulting from industrial smelting in the Swedish firm SSAB (Oxelösund). The chemical composition of the investigated steels is to be seen in Table 1. The material was supplied in the form of steel sheets, with a thickness of 20 mm (Weldox 900) and 10mm (Weldox 1300). These sheets were sampled for anodic dissolution (Ø7 mm and Ø15 mm and the length 40 mm) and measurements of their hardness and for metallographic investigations. The hardness of steel Weldox 900 in the delivered state amounts to about 34 HRC, and that of Weldox 1300 to about 48 HRC. Metallographic observations have revealed in these steels a fine dispersive structure of tempered martensite with various morphologies (Fig. 1) and varied tractability for etching of the matrix α'(M) [14-15].

Electrochemical investigations comprised the determination of the active potential of dissolution of the investigated steels in various chemical reagents (Table 2) and anodic dissolution both by means of the chronopotentiometric method (at a constant current) and the chronoamperometric method (at a constant potential [16-17].

The dissolution of electrochemically active phases in a given electrolyte solution was controlled potentiostatically by keeping the given potential versus the reference electrode (saturated calomel electrode, SCE). For this purpose curves of anodic polarization I=f(E) were plotted determining the dependence of the rate of dissolution on the assumed potential, and the ranges of active dissolution and anodic passivation of the metal were found. The dependence permitted to determine the potentional, at which the ratio of the dissolution rate of the matrix versus the precipitation reaches the highest values [18-19].

a)



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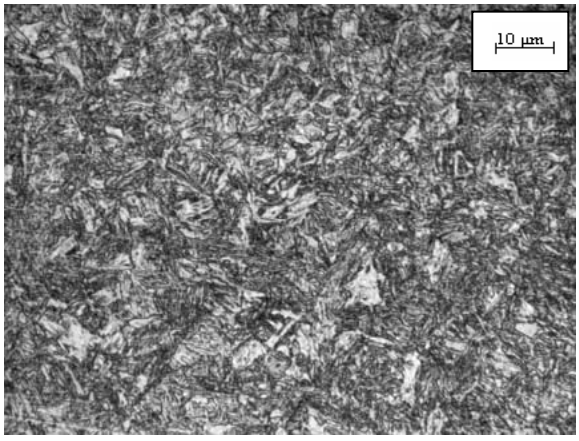

Fig. 1. Structure of the investigated steels in the delivering state; central surface of sheet metal; a) Weldox 900, b) Weldox 1300

The anodic polarization curves of the investigated steels were determined potentialdynamically making use of a glass electrolyzer (Fig. 2) and a PGP 201 potentiostat from the firm Radiometric Copenhagen which is a part of the system VoltaLab21 cooperating with the personal computer.

The curves of anodic polarization determined for various solutions are to be seen in Fig. 3.

Chronoamperometric and chronopotentiometric curves of the anodic dissolution of Weldox 1300 steel in the investigated solutions have been presented in Figs. 4. and 5.

X-ray investigations of electrolytic extractions were run by means of an X-ray diffractometer type XRD 7, produced by Seifert-FPM, applying the radiation of an anode λCoK_{α} and a Fe - filter. Electrolytic extractions, deposited on a filter paper were analyzed within the range of angles $^{o}2\Theta$ from 10^{o} to 110^{o}. The step-scanning method was used at a step value of $0.1^{o}2\Theta$ and a time of measurements amounting to 7 seconds in one measurement position. The obtained diffraction patterns were analyzed applying the program Diffract AT Search/Match.

Corrosive investigations of Weldox steels were carried out by means of the potentiostatic method, applying the electrolytes gathered in Table 3 and a calomel electrode as a reference electrode.

Table 1.
Chemical composition of the investigated steels

Kind of steel	Kind of analysis	Chemical composition, % by weight														
		C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al	Nb	V	Ti	N	B
Weldox	by certificate	0.20	0.50	1.5	0.020	0.010	0.7	0.02	0.7	0.03	0.018	0.04	0.06	0.04	0.05	0.005
Weldox		0.12	0.21	0.90	0.007	0.001	0.48	1.23	0.40	0.01	0.038	0.02	0.02	<0.01	0.06	0.005

Table 2.
The composition of electrolyte–solutions applied for the anodic dissolution of the investigated steels by PN 64/H-04510

Designation of electrolyte	Chemical composition of solutions
1	50 g sodium cirate, 20 g citric acid, 10 g potassium iodide, 1000 ml distilled water.
2	300 g iron ammonium sulfate, 1000 ml distilled water.
3	10% concentrated hydrochloric acid in 1000 ml distilled water.

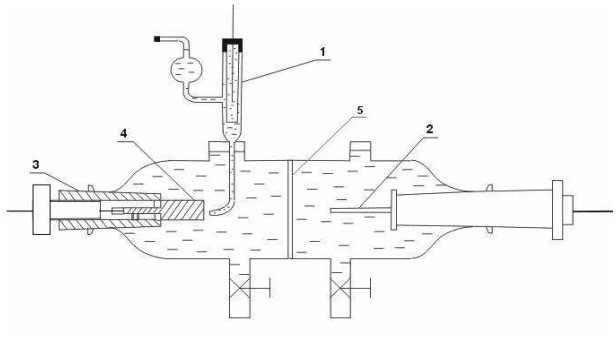

Fig. 2. Diagram of an electrolyzer for the anodic solution of Weldox steels: 1-Haber-Ługin capillary with a reference electrode, 2-auxiliary electrode (cathode), 3-holder of the tested electrode, 4-sample (anode), 5- diaphragm made of sinter glass

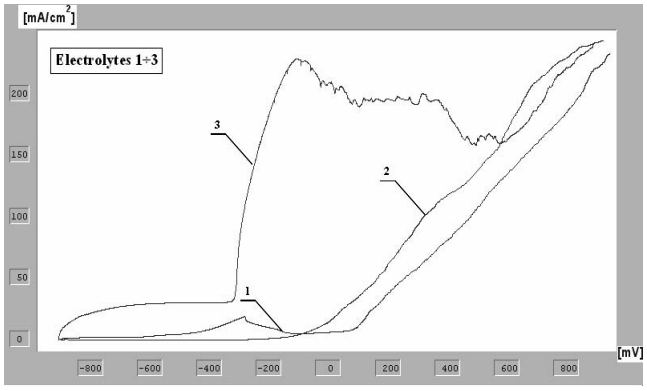

Fig. 3. Potentiodynamic curves of the anodic polarization for Weldox 1300 steel obtained by the method of linear voltamperometry for various electrolytic solutions

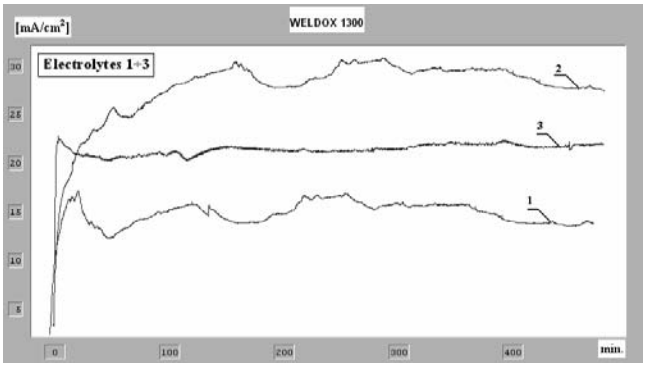

Fig. 4. Chronoamperometric curves of the anodic polarization for Weldox 1300 steel in various electrolytic solutions

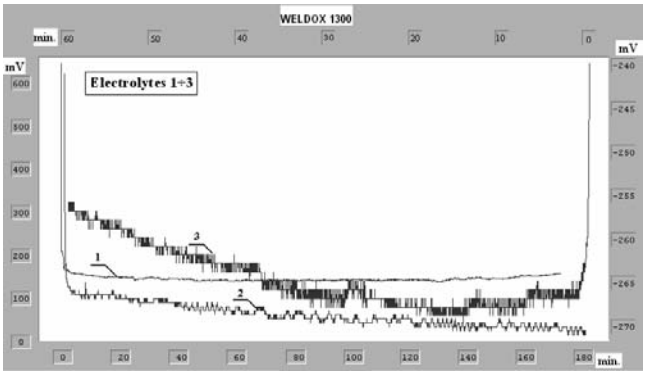

Fig. 5. Chronopotentiometric curves of the anodic polarization for Weldox 1300 steel in various electrolytic solutions

Table 3.
Chemical composition of electrolytes used for tests of the corrosive resistance according to PN-78/H-04608

Designation of electrolyte	Chemical composition of solutions
4	30 g sodium chloride, 1000 ml distilled water.
5	10% concentrated hydrochloric acid in 1000 ml distilled water.
6	100 g sodium chloride, 3.646 g hydrochloric acid, 1000 ml distilled water.

3. Results and discussion

The acquaintance of phenomena proceeding during the electrochemical dissolution of high-strength constructional steels conditions the good quality of the extraction as well as a correct estimation of the corrosion resistance of steel in a defined environment. Extractions are obtained by the anodic dissolution of massive samples at a controlled electrochemical potential [20-21]. In effect, the dissolved metal is transformed during the electrolysis into ions dissolved in the electrolyte. In the case of steels the iron undergoes anodic dissolution, whereas the other phases form an undissolved anodic deposit, which is the final product for X-ray phase analysis. Essential is the composition of the solution applied in the process of dissolving the steel samples and its pH, because iron can be dissolved anodically as simple ions Fe^{2+} and Fe^{3+}. The dissolution of iron is a process of electrochemical oxygenation and it runs on a grid electrode according to the reaction [22]:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (E = -0.44\ V) \tag{1}$$

$$Fe^{3+} + 3e^{-} \rightarrow Fe \quad (E = -0.04\ V) \tag{2}$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (E = +0.77V) \tag{3}$$

The resolutions of electrolytes applied in the process of anodic dissolutions were chosen from the viewpoint of the value of the stationary potential of electrochemical iron as well as the pH value. The activity of electrolytes in the process of dissolution in the investigated Weldox steels was assessed basing on the loss of the dissolved specimen, the precipitated anode deposit and the time of dissolution (Table 4.).

It has been found that the solution No. 3 is the most effective electrolyte dissolving Weldox 1300 steel, with respect to the mass of the obtained electrolytic extraction versus the mass of the dissolved specimen. This solution is also most effective due to the rate of dissolving the sample. In the case of applying the chronopotential method Weldox 1300 is faster dissolved in the electrolyte No. 1. Anodic dissolution of Weldox 900 runs fastest in the solution No. 3 which is also the most effective solution with respect to the obtained mass of electrolytic extraction.

The results of the X-ray phase analysis of the obtained electrolytic extractions have been gathered in Tables 5 and 6. and also in the X-ray diffraction patterns (Fig. 6). The separate phases have been identified making use of the comparative method based on the ICDD files of the year 1999.

Basing on the identification of the diffraction lines it has been found that in the investigated steels following phases may occur:

- carbides and nitrides type NbC, $Nb_4N_{3,92}$ – in Weldox 1300 steel,
- nitrides type AlN, BN, Mn_2N_3, as well as particles α-Fe and probably FeOOH, as a product of secondary electrolytes reaction – in Weldox 900 steel.

It has been found that the received results of electrochemical and X-ray examinations depend essentially on the kind of the electrolyte solution applied for the dissolution of the investigated Weldox steels.

This suggests a distinct dependence of the mass and kind of the dissolved phase on the value of the electrochemical potential and the active or passive state of the surface of the dissolved steel versus SCE.

On the basis of electrochemical examinations of corrosion resistance, it has been found, that steels of the Weldox type demonstrate a considerable corrosion resistance both in electrolytes simulating a large saline environment and acid environment. Steel Weldox 1300 shows a higher electrochemical corrosion resistance in comparison with steel Weldox 900 in the investigated electrolytes. Electrolyte No. 4 (Table 3.) is the least invasive corrosion environment, in which Weldox 1300 is classified to the group of entirely corrosion resistant steel, and steel Weldox 900 - to the group of steel with a high corrosion resistance. The investigated Weldox steels in electrolytes No. 6 display a smaller electrochemical corrosion resistance. Electrolyte No. 5 is the most destructive environment, in which the investigated steels are little resistant to electrochemical corrosion.

Table 4.
Results of the anodic dissolution of Weldox steel

Kind of the steels	Extraction's method	Designation of electrolyte	Reduction of mass of the specimens [g]	Mass of the obtained isolate [g]	Time of dissolution [min.]
Weldox 1300	Chronoamperometric	1	2.2796	0.0001	1640
		2	2.4662	0.0002	1180
		3	4.4174	0.1106	1030
	Chronopotentiometric	1	3.1625	0.0001	300
		2	3.4411	0.0001	390
		3	5.6805	0.1348	670
Weldox 900	Chronopotentiometrric	3	3.6701	0.5394	270

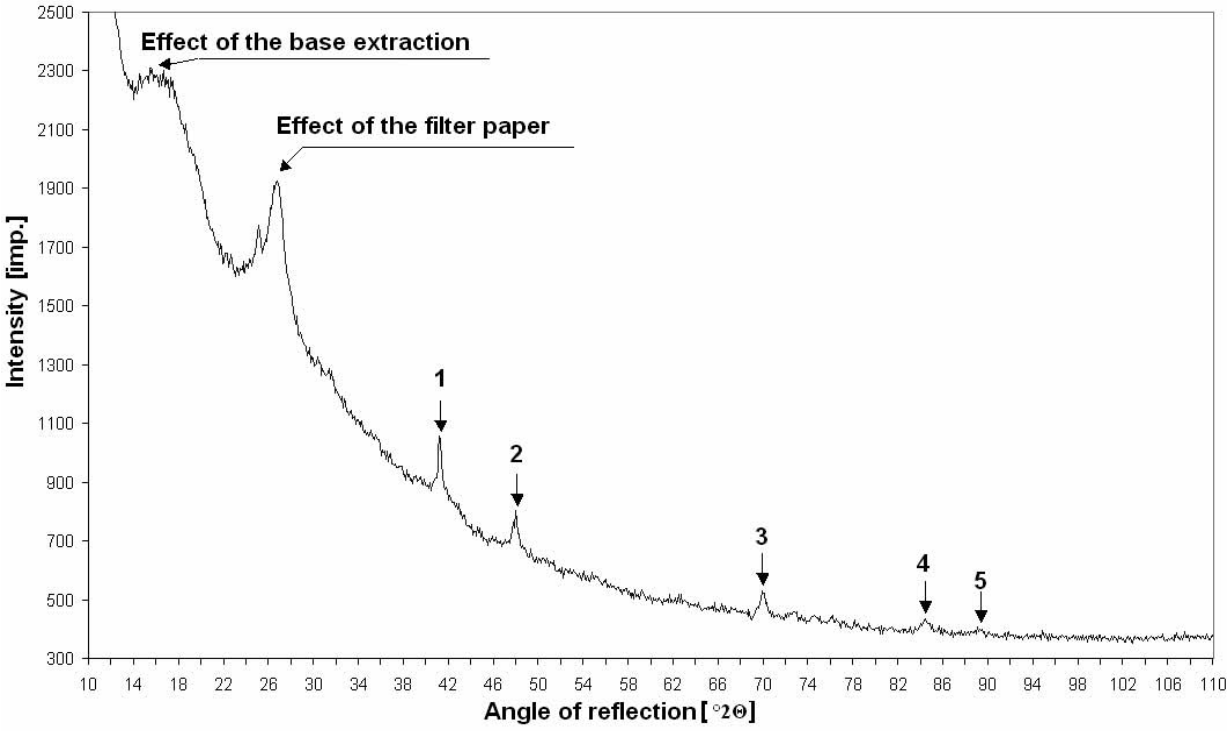

Fig. 6. X-ray diffraction patterns of electrolytic extractions from Weldox 1300 steel anodic alloy dissolved in the reagent N°3; 1-5 analyzed diffraction line

Table 5.
Results of X-ray phase analysis of the electrolytic extractions of Weldox 900 steel

N°	Evidence				Identified phase according to ICDD													
	Angle of reflection		d_{hkl} Å	I/I_0	AlN 32-679			BN 26-773			Mn_2N_3 1-1158			α-Fe 6-0696			FeOOH 26-792		
	°2Θ	°Θ			d_{hkl} Å	I/I_0	hkl	d_{hkl} Å	I/I_0	hkl	d_{hkl} Å	I/I_0	hkl	d_{hkl} Å	I/I_0	hkl	d_{hkl} Å	I/I_0	hkl
1	31.3	15.65	3.3182	16													3.30	100	110
2	41.4	20.7	2.5223	19													2.554	80	101
3	42.1	21.05	2.3639	13	2.385	100	311												
4	44.9	22.45	3.3440	26															
5	46.8	23.4	2.2538	10	2.287	10	222												
6	47.8	23.9	2.2094	12				2.211	100	100									
7	50.5	25.25	2.0984	22				2.114	70	002	2.10	33	200				2.213	80	020
8	52.2	26.1	2.0346	100							2.02	20	002	2.0268	100	110	2.020	60	120
9	54	27	1.9716	18	1.980	60	400	1.959	45	101									
10	58	29	1.8463	13															
11	61.5	30.75	1.7507	6													1.747	100	211
12	65.4	32.7	1.6569	8													1.649	80	220
13	66.5	33.25	1.6325	10	1.6169	15	422												
14	68.9	34.45	1.5823	10				1.528	18	102							1.542	60	310
15	73.3	36.65	1.4995	8	1.5250	35	511				1.48	13	220				1.496	60	002
16	77	38.5	1.4379	22	1.4000	85	440				1.45	25	202	1.4332	20	200	1.442	80	301
17	93.9	46.95	1.2249	19				1.2770	25	110	1.22	5	113						
18	100.8	50.4	1.1617	12				1.1880	16	103				1.1702	30	211			
19	104.4	52.2	1.1328	6															
20	105.1	52.55	1.1275	5															

Table 6.
Results of the X-ray phase analysis of the electrolytic extractions of Weldox 1300 steel

Line Number	Evidence				Identified phase according to ICDD		
	Angle of reflection		d_{hkl} Å	I/I_0	$Nb_4C_{3,92}$ 34-337		
	º2Θ	ºΘ			d_{hkl} Å	I/I_0	hkl
1	41.3	20.65	2.5382	100	2.5364	100	111
2	48	24	2.2007	61	2.1965	81	200
3	70	35	1.5606	66	1.5533	43	220
4	84.4	42.2	1.3326	22	1.3249	29	311
5	89.5	44.75	1.2714	16	1.2685	12	222

4. Conclusions

1. High - resistant microalloyed constructional Weldox 900 and Weldox 1300 steels in the delivered state demonstrate a structure of tempered martensite with various morphologies and varied tractability for etching of the matrix α'(M). The hardness of the investigated steels Weldox 900 in the delivered state amounts to about 34 HRC, and that of Weldox 1300 to about 48 HRC.
2. Electrochemical dissolution of steels type Weldox 900 and Weldox 1300 in the delivering state is an effective method of separating an adequate mass of electrolytic extractions for qualitative X-ray phase analysis.
3. The most favourable reagent used for anodic dissolution of the investigated steels is an electrolyte on the basis of 10% of aqueous solution of hydrochloric acid.
4. The chronoamperometric method ensures a twice larger mass decrement of the sample than the chronoamperometric method in a comparable time of the process.
5. The analyzed steels display a high corrosion resistance to the destructive effect of a saline environment and a low resistance to an acid environment. In steel Weldox 1300 comparison with steel Weldox 900 ensures a twice higher corrosion resistance, both in saline and acid environments.

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