INFLUENCE OF REDUCING SALT BATH TO STAINLESS STEELS PICKLING

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Abstract

The reason for application of reducing salt bath pickling technology prior to the acid pickling technology is better solubility of the low valent metal oxides and metals, especially for high-alloy steels and alloys. The results of the Glow Discharge Optical Emission Spectroscopy (GDOS) and chemical analysis of the scales by Scanning Electron Microscope of the high alloy steel before and after the treatment of the reducing salt bath will be presented. The paper will be completed by the results of the practical tests of materials with variable chemical composition with reducing salts.

Key words*: reducing salt, pickling acid, scale.*

1. Introduction

Creation of oxidic layers, so-called scales, takes place on metal surfaces during a hot forming, thermal processing and welding. Scale chemical composition depends mainly on steel chemical composition as well as on the forming temperature, composition of furnace atmosphere, temperature and time of annealing, system of cooling, etc. The scales have different mechanical properties (hardness, brittleness) in comparison with the matrix. It impedes subsequent forming procedures (for example rolling, drawing) and therefore they must be removed.

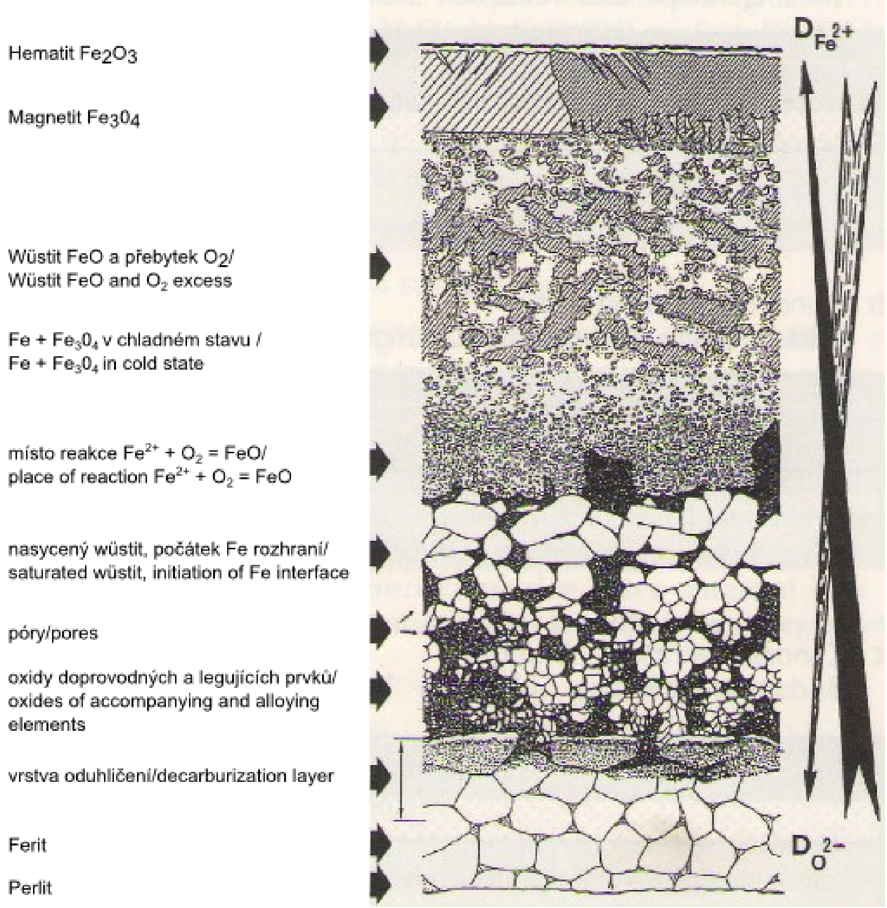
If a good corrosion resistance must be secured after the final processing, the scale removing is absolutely necessary.

Chemical methods are used the most frequently for the scale removal. The scales are dissolved in solutions of inorganic acids – pickling – with the creation of metallic salts. The process (mechanical, chemical) that facilitates or accelerate the pickling process is often carried out before the pickling itself [1].

Pickling is generally a basic and the most frequently used procedure of steel surface treatment that influences fundamentally both subsequent technological processes (forming), surface treatment processes (galvanizing, application) and corrosive behaviour of the metals. It is used mainly as an interstage procedure between the hot and cold steel forming (hot pickling as well as cold pickling of rolled strip, pickling of rolls of wires, tubes and bars, etc.). It is stated that out of the total world production of steel from 60 to 70% of the material is pickled at least once during the production cycle. The pickling is a complicated electro-chemical process, in which many chemical and electro-chemical processes take place. These processes are initiated by a creation of local electro-chemical cells between metal oxides and basic metallic matrix in acidic electrolyte. Dissolution, possibly separation of oxidic layer takes place and part of the matrix adjacent to the scale layer is dissolved at the same time. The pickling solutions are diluted inorganic acids or their mixtures with addition of other substances. Their compositions differ depending on the steel composition [1].

Hydrochloric acid (HCl) and not so frequently also sulphuric acid (H_2SO_4) are used for carbon steel pickling nowadays. Other pickling solutions are used only very rarely.

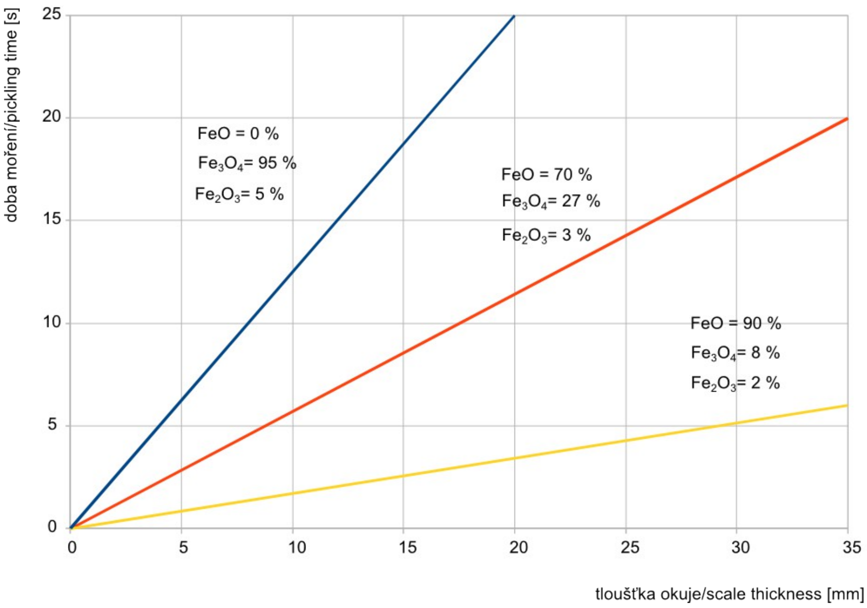
Figure No. 1 shows a schematic structure of the scale at carbon unalloyed steel [1]. Thicknesses of individual phases of the scale layer range from 5 to 50 µm. All phases including layer with removed carbon must be removed during the pickling. Alloying elements that gather above the metallic matrix behave differently during the annealing depending on their affinity to oxygen and ability of diffusion through the lattice. Also insoluble elements or elements with a difficult dissolving in acids gather there (C, Si and their binary compounds with metals that further worsen the picklability of the steels).



Obr. 1: Schematické znázornění stavby okujové vrstvy vytvořené v oxidační atmosféře na ocelovém povrchu uhlíkové, nelegované oceli.
Figure 1: The model of the structure of scale layer created in oxidation atmosphere on the surface of carbon no-alloy steel.

2. Relation between Picklability and Scale Composition – Carbon Steels

Scale of carbon unalloyed steel contains mainly iron oxides. Chemical composition of the scale, its thickness and porosity influence the steel picklability significantly. The pickling procedure is the fastest, if the scale contains a maximum amount of wüstite (FeO), certain amount of magnetite (Fe_3O_4) and minimum amount of hematite (Fe_2O_3). It means from the practical point of view that **the oxide that is the best soluble in acids is the oxide with the lowest valency of metal** – wüstite. **Solubility of** iron oxides **decreases with the increasing valency.** Even wüstite is less soluble than the fundamental matrix. Graphical confirmation of this affirmation is on the Figure No. 2 [1]. Three types of the scales with different chemical compositions on the surface of cold rolled strip were pickled in hydrochloric acid and times of pickling were compared. The scale containing the biggest amounts of iron oxides with the highest valency had the longest pickling time. It means for the practical application that for example scale breaker, blasting machine or smoothing rolling with a minimum reduction securing erosion or removal of hematite layer is placed before the pickling in case of the device for the strip pickling. Creation of the scale that is suitable for the pickling by means of a modification of the annealing atmosphere during previous thermal processing or by a suitable cooling [1] is another possible variant.



Obr. 2: Závislost doby moření na složení a tloušťce okuje.
Figure 2: The relation between the time of pickling and scale thickness.

3. Pickling of Corrosion-resistant Steels and Alloys

The corrosion-resistant (high-alloy, high-grade) steels are the steels with higher contents of alloying elements, mainly Cr and Ni. Thanks to their composition these steels have higher chemical resistance, strength and thermal stability (acid-resistant, fire-resistant, fire-strength). Of course the pickling is more difficult in this case. It is said generally that the pickling time of the alloyed steels is up to 10 times longer in comparison with unalloyed steels and the used pickling media must be different and more aggressive.

We distinguish the following steels according to the lattice structure:

austenitic (Cr 16 – 35 %, Ni 7 – 26%, Mo < 6 %, C < 0.12 %, N2 < 0.5%, Cu, Mn, S),
ferritic (Cr 13 – 30 %, C < 0.1%, Si < 1 %, Mo < 4.5 %),
martensitic (Cr 12 -18 %, C 0.05 – 1.2 %, Ni < 7 %, Mo up to 3 %, Ti),
duplex (Cr 19 – 28 %, Mo < 5 %, Ni < 7 %).

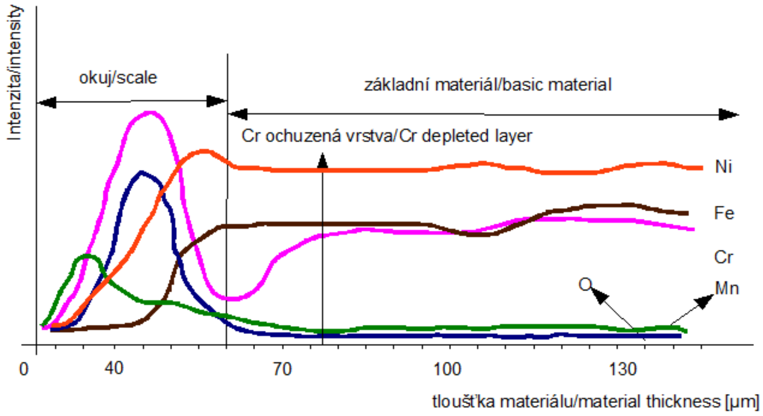
The steels are also alloyed by other metals in order to prepare other properties, or to improve the existing properties of the steel. Of course there is a change of the scale layer composition, or composition of the matrix adjacent to the scale layer after the change of the steel chemical composition.

In addition to the iron oxides the scale contains also oxides of alloying elements **Cr**, **Ni**, **Mn**, V, Ti, Mo, **Al, Si** and Cu. Besides pure oxides the lattice contains also mixed oxides – spinels / **$(Me^{II+}O)$. $(M^{III+}{}_2O_3)$**/ – where Me and M are metal generally. No unambiguous dependence exists between the thickness and composition of the scale layer on one side, and temperature, time of thermal processing and atmosphere composition on the other side. Certain relations between the composition of the basic material and scale composition exist, which influence significantly the picklability of the steels. The pickling technology (acid, acid mixture) can be designed according to the steel composition. It is also possible to propose a suitable pre-treatment that can facilitate, possibly accelerate the pickling process. Type of the pickled product is also very important – strip, wire, tubes, bars, etc. Another point of view is the fact, if the process is an interstage or final treatment of the product [1, 2].

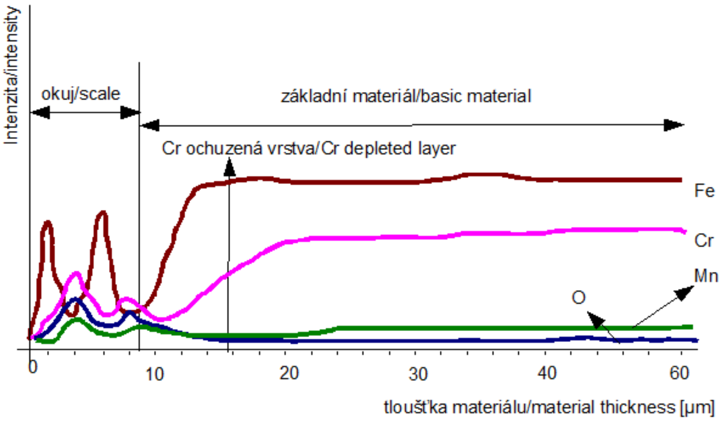
4. Influence of Elements on Scale Structure

Chromium influences **markedly the scale composition** and **picklability of highly alloyed steels**. Chromium diffuses from the metallic matrix up to the highest layers during the scale creation. Oxygen diffuses in an opposite direction and because affinity of chromium against oxygen is very high, a layer of chromium oxide is created on the surface that contains only small amounts of Fe and Ni. Mn behaves the same way like Cr. Inner layer of the scale does not contain so high amount of chromium oxide, but it contains spinels and places with higher concentrations of Si and Al. Matrix depleted on chromium is placed under the oxidic layer. This layer must be also removed by pickling [1, 2] because of its lower corrosion resistance.

Uncontrolled conditions during the thermal processing can cause fluctuation of thickness and composition of the scale. Conditions for a controlled creation of a scale with a better picklability can be created during the strip processing (temperature, atmosphere, cooling). This procedure is more complicated in case of wire coils. Wire scale thickness is 20 up to 100 times bigger in comparison with strip. Scale thickness of austenitic wires 18/9 at the temperature from 1040 to 1065 ^{0}C and annealing time from 30 to 60 minutes is from 13 to 23 μm. The scale thickness of AISI 430 at the same temperature, time of annealing and temperature from 790 to 845 ^{0}C is from 12 to 17 μm. General conclusion – there is no unambiguous dependence on temperature, time of annealing and oxygen content in the atmosphere for the scale thickness of the wires. GDOS method was used for monitoring of in-depth profile of element distribution in the scale and in the matrix of the wires made from austenitic and ferritic steels. The course is displayed on the Figures No. 3 and 4.



Obr. 3: Schematické rozložení prvků na povrchu austenitické oceli (AISI 304).
Figure 3: The model of the elements distribution on the surface of austenitic steel (AISI 304).



Obr 4: Schematické rozložení prvků na povrchu feritické oceli (AISI 430).
Figure 4: The model of the elements distribution on the surface of ferritic steel (AISI 430).

We can see a distinct increasing of chromium content in the scale layer of austenitic steel AISI 304, whereas its curve corresponds exactly with oxygen content, which confirms its high affinity to the oxygen. Manganese behaviour is also very interesting. Its diffusion is comparable with chromium. So the surface layer of the scale is created by chromium and manganese oxides with very low solubility. Iron gets to the surface layer only at minimum amount. Nickel enriches only the part of the scale layer adjacent to the matrix.

Ferritic steel AISI 430 has a completely different distribution of elements in the scale. Surprisingly in this case the upper layer contains a bugger amount of iron and only the phase below it contains a mixture of chromium and manganese oxides. Further phase enriched by iron is created towards the matrix and phase of chromium and manganese oxides is placed close to the matrix. This distribution corresponds probably with the thermal processing of the relevant sample.

5. Procedures Used for Pickling of Highly Alloyed Steels

The most frequently used acids for the pickling of the highly alloyed steels are as follows: hydrochloric acid (HCl) and sulphuric acid (H_2SO_4), but above all mixtures of nitric acid (HNO_3) with hydrofluoric acid (HF), or sulphuric acid (H_2SO_4) with hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2).

The procedures that can accelerate the process are used before the acids in order to **accelerate and improve** the pickling:

Mechanical scale removal (blasting, breaking, bending) – wire coils, strip

KMnO4 + NaOH (ferritic steels) – wire, tubes

Electrolysis in solutions of Na2SO4 , NaOH, H2SO4 - strip

Electrolysis in melts (NaOH, KOH)

Oxidation melt (NaOH, NaNO3, KNO3, Na2B4O7),

Reducing melt (NaOH, NaH).

The above-mentioned processes cause physical or chemical changes of the scale and the subsequent pickling in the acids or mixtures is more effective. Shorter exposition times in the acids, possibly lower concentrations or temperatures of the acids decrease weight losses during the basic metal dissolution.

6. Pre-pickling in Reducing Melt

Melted and dewatered sodium hydroxide containing a reduction component of sodium hydride (NaH) is used as reducing hydride melt for surface treatment of the highly alloyed steels and alloys. Sodium hydride is supplied into the melt in a form of Feropure concentrate (13 – 16 % NaH) and it is kept in the reducing melt in concentrations, in which it is capable to reduce partly the scale layer. Sodium hydroxide that is a carrying component of the melt reacts with most of the metals (Fe, Cr, Ni, Cu, Nb, Mn, W, Mo, Si) in the steels. Also oxides of these metals, if they are parts of the scale layer dissolve in NaOH melt at a minimum level and only in case of a long-term action. Metals and their oxides that react chemically with sodium hydroxide (for example Zn, Al, Ti) and create complex oxo-anions are the only exceptions.

Capability of metal oxide reduction in the scale layer is fundamental in case of application of the reducing hydride melt. Sodium hydride in the melt reduces some oxides in the scale layer and the level of the scale layer reduction can be characterized by a difference of the oxygen content in the scale layer before and after the exposition in the melt.

These are principally two types of reduction reactions according to the following general equations 1 and 2:

$$\mathbf{Me_aO_b\ (s) + b\ NaH = a\ Me + b\ NaOH} \quad (1)$$

$$\mathbf{Me_aO_b\ (s) + c\ NaH = Me_aO_{b-c} + c\ NaOH} \quad (2)$$

Reducibility of simple metal oxides by sodium hydride decreases in the line **NiO - CoO - CuO - FeO (Fe_3O_4) – Mn_2O_3 – Cr_2O_3 – V_2O_3 – TiO_2.** Reduction of nickel, cobalt, copper and iron is the easiest one and the reduction goes up to the metal. Manganese creates a turning point in the reduction. Its higher oxides reduce only to MnO. Chromium is the next element and its oxides reduce only partly to CrO in the conditions of the reducing melt [3, 4].

It is valid generally that the hydroxides and oxides of the same element in various oxidation states differs noticeably by their acidobasic properties. Hydroxide or oxide at a lower oxidation state is always more alkaline and it is therefore also more soluble in acids. Solubility of pure metals in acids is even higher because of electro-chemical reasons [5].

Long-term practical application of the reducing melts has proved their general-purpose chemical capability to prepare the scale layer for its simple, faster and more effective pickling process.

Mixture of HNO_3 and HF is used the most frequently for the high-grade steel pickling. Hydrofluoric acid is a weak acid with a strong tendency to creation of complex fluorides of metals. Nitric acid is a strong acid with oxidizing properties that passes easily to various oxidizing and reducing forms. Course of the reactions of oxidic layer with the acid mixture is as follows: Dissolving of metal oxides and basic matrix depleted on chromium by nitric acid takes place during the first stage and it is followed by a transfer of dissolved metals to fluoride complexes by the reaction with HF. Solubility of these complexes decreases with an increasing concentration of complex fluorides and they start to precipitate in a form of sludge.

Nitric acid is used for austenitic steels in concentrations from 14 to 16 weight % in a mixture with 3 – 5 % HF at the temperatures up to 50 ^{0}C. The mixture secures the best dissolving of iron and chromium. It enables an easy creation of fluoro-complexes of iron and chromium and it is the reason of an easy pickling of ferritic or mertensitic steels in the mixtures of these acids. Higher contents of HF support a dissolving of the basic matrix; lower contents keep a small speed of the pickling. Lower concentrations and temperatures of the acids (8 % HNO_3 + 1 – 3 % HF at 40 ^{0}C), or for example 10 % HNO_3 + 0.7 – 1 % HF either at the temperature of vicinity, or even cooled (exothermic reaction) Are used for the pickling of ferritic and martensitic steels.

The pickling of austenitic, ferritic and martensitic steels takes place also in the mixtures of H_2SO_4 and HF. The mixture must have a dissolving ability for metals and metal oxides that has been increased by an addition of oxidizing component (hydrogen peroxide, aeration). These mixtures are more suitable from the ecological point of view (emissions, absence of soluble nitrates), but they are not so universal for the pickling of the highly alloyed steels as the mixtures of HNO_3 and HF. The combination with the reducing melt increases number of steel types (ferritic, martensitic) that can be pickled.

7. Testing of Steel and Alloy Surfaces with Application of Reducing Melt

Testing of the surfaces of selected steels and alloys with the application of the reducing melt as the first step of pre-treatment with a subsequent acid pickling was carried out experimentally. Comparison of the reduction at a higher concentration of NaH (about 2 % by weight) and technological concentration (0.2 – 0.3 % by weight NaH) was used in some cases.

Determination of chemical composition of the scale layer on the wires at various stages of surface treatment (initial state, after action of the reducing melt and after pickling in acids) was the main target of the testing. The scale layer was evaluated at cross section by means of scanning electron microscope (SEM). It included a documentation of the scale layer from various places on the wire circumference, semiquantitative X-ray microanalysis and measurement of the scale thickness. The microanalysis evaluated different parts of the oxidic layer and also basic material up to the depth of 20 to 40 μm below the surface. Semiquantitative X-ray microanalysis of the matrix was carried out for a comparison. Observation of the scale layer was carried out by the scanning electron microscope JEOL JSM-6490LV in reflected electrons (BE) The semiquantitative X-ray microanalysis was carried out by analyser Inca X-act as surface analysis.

The samples were processed according to the following procedure:

1. Sample weighing, photo documentation, surface analysis by scanning electron microscopy.
2. Sample exposition in reducing melt (temperature 410 °C, NaH concentration 0.22 – 0.32 weight %, possibly 2 weight %), cooling and rinsing by water, drying.
3. Sample weighing, photo documentation, surface analysis by scanning electron microscopy.
4. Final surface treatment in selected acids, rinsing by water, drying.
5. Sample weighing, photo documentation, surface analysis by scanning electron microscopy.

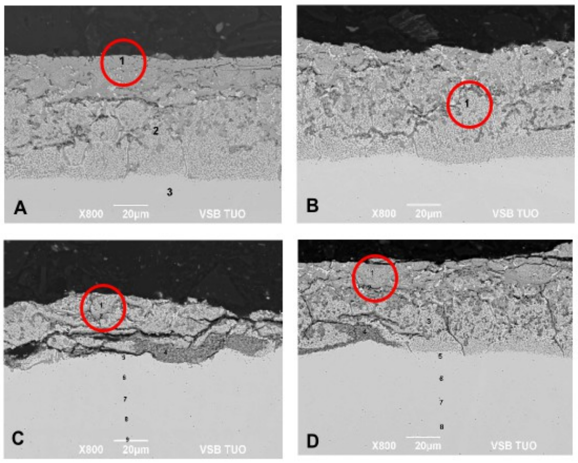
8. Results and Discussion

Austenitic steel AISI 304 was exposed for shorter and longer time in the reducing melt with a usual composition (0.22 % NaH) and in the melt with a higher content of NaH (2 %).

Chemical analyses of elements were carried out at the marked places – Figure No. 5. Chemical composition of the evaluated material according to the standard is shown for a comparison in the first line of the Table. Subsequently this diagram is valid also for other samples.

The results of the oxygen content measurement showed that both the length of exposition in the melt and by one order higher concentration of NaH **do not influence noticeably** the reducibility of the scale layer. It is obvious that the presence of a higher content of iron in the scale has a fundamental influence of the scale reducibility (chromium oxide can be reduced only with difficulties). Element analyses of the input sample surface shows (Figure No. 3) that Mn diffuses slightly more to the scale layer in comparison with Cr and the oxygen content curve corresponds with the chromium content curve in the scale layer. The scale layer adjacent to the matrix enriches by Ni slightly.

AISI 304 (austenická struktura/austenitic structure)



%	–	1,5	0,6	18,0	70,0	10,0
	O	Mn	Si	Cr	Fe	Ni
A	34,0	1,5	–	14,4	49,6	0,5
B	21,7	1,0	–	20,0	43,8	13,6
C	25,2	1,2	–	22,7	37,3	12,4
D	25,0	1,1	–	21,5	34,9	17,1

Obr. 5: Charakter okujové vrstvy oceli AISI 304 a její chemické složení [hm. %] po moření v redukční tavenině. A – výchozí stav, B – stav po redukční tavenině (5 min, 0,22 % NaH), C – stav po redukční tavenině (3 h, 0,22 % NaH), D – po redukční tavenině (15 min, 2% NaH).

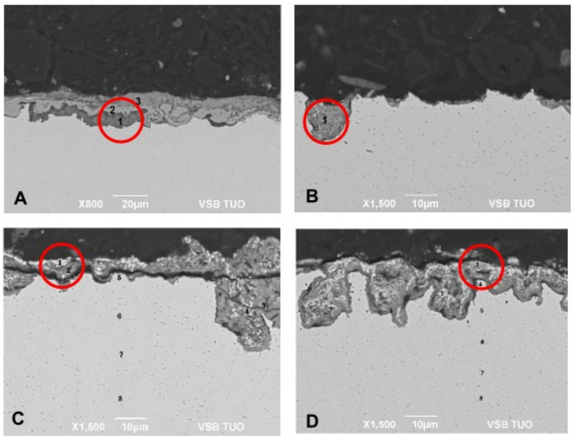
Figure 5: The character of the scale layer of steel AISI 304 and its chemical composition [wt. %] after pickling in reducing salt. A – initial state, B – state after reducing salt (5 min, 0,22 % NaH), C – state after reducing salt (3 h, 0,22 % NaH), D – state after reducing salt (15 min, 2 % NaH).

Ferritic steel AISI 430 was exposed in the melt at the same conditions like the austenitic steel. The scale layer has a different composition and its behaviour during reduction is different (Figure No. 6). Multiphase structures of oxides (Figure No. 4) are created in the scale layer, whereas two phases with higher content of Fe and lower content of oxygen surround the interphases of Cr and Mn with higher oxygen content. Behaviour of the samples during the reduction is very interesting. We can see by comparison of the shorter and longer exposition on the melt at a standard conditions that layer of metallic Fe with minimum content of Cr is created during the longer exposition (3 hours). This is probably supported by an original structure of the layer. There is a noticeable decrease of oxygen content in the scale after the exposition in the melt with a higher content of NaH (by order). This is probably related to the local higher content of Fe and non-reducibility of chromium oxide.

We also present reductions of scale layers on alloys with different chemical compositions.

Alloy containing **61 % Ni, 23 % Cr, 14 % Fe and 1.4 % Al** is practically non-picklable in acids. A continuous oxidic phase containing predominantly chromium oxides is on the surface (Figure No. 7) at the initial state. The layer also contains Fe, Ni, Ti and Al in the amount of 6 % by weight. The oxygen content decrease by 20 % takes place during the reduction on the melt. The subsequent pickling in the acid enables to obtain a clean surface without any oxides. The scale layer cannot be removed completely from this alloy without the melt.

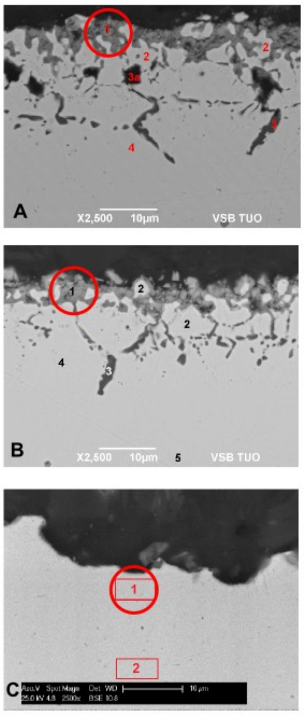
AISI 430 (feritická struktura/ferritic structure)

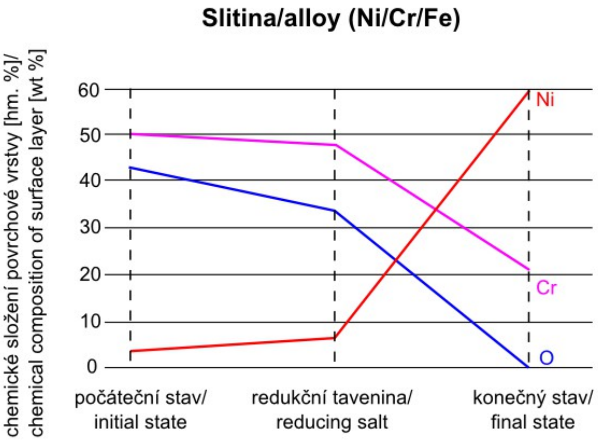


%	—	1,5	0,6	18,0	70,0	10,0
	O	**Mn**	**Si**	**Cr**	**Fe**	**Ni**
A	37,0	2,7	0,4	34,0	22,6	0,9
B	22,8	2,1	0,3	16,9	54,8	—
C	—	—	—	1,5	98,5	—
D	12,9	1,4	—	4,3	79,5	—

Obr. 6: Charakter okujové vrstvy oceli AISI 430 a její chemické složení [hm. %] po moření v redukční tavenině. A – výchozí stav, B – stav po redukční tavenině (5 min, 0,22 % NaH), C – stav po redukční tavenině (3 h, 0,22 % NaH), D – po redukční tavenině (15 min, 2% NaH).

Figure 6: The character of the scale layer of steel AISI 430 and its chemical composition [wt. %] after pickling in reducing salt. A – initial state, B – state after reducing salt (5 min, 0,22 % NaH), C – state after reducing salt (3 h, 0,22 % NaH), D – state after reducing salt (15 min, 2 % NaH).



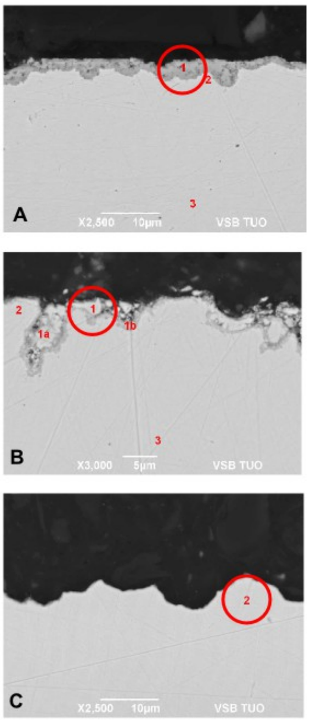


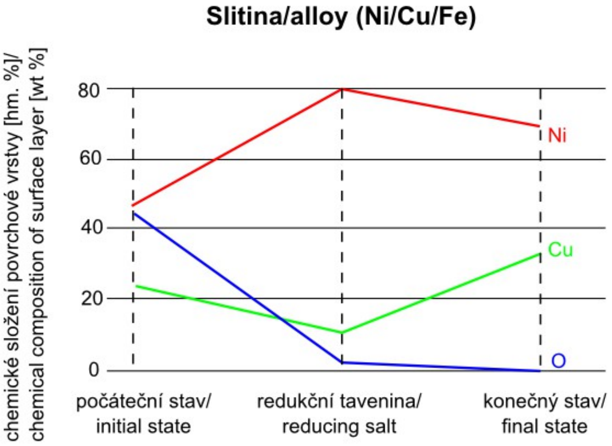
%	—	1,4	—	23,0	14,0	61,0	—
	O	**Al**	**Si**	**Cr**	**Fe**	**Ni**	**Ti**
A	42,7	0,9	—	50,2	1,1	2,9	2,2
B	34,4	0,9	—	46,6	3,6	6,0	2,2
C	—	0,8	0,5	20,5	14,7	63,5	—

Obr. 7: Charakter okujové vrstvy slitiny Ni/Cr/Fe a její chemické složení [hm. %] po moření v redukční tavenině a následném domoření v kyselině. A – výchozí stav, B – stav po redukční tavenině (30 min, 0,22-0,32 % NaH), C – stav po domoření v kyselině (HNO3 + HF).

Figure 7: The character of the scale layer of alloy Ni/Cr/Fe and its chemical composition [wt. %] after pickling in reducing salt and subsequent pickling in acid. A – initial state, B – state after reducing salt (30 min, 0,22-0,32 % NaH), C – state after subsequent acid pickling (HNO_3 + HF).

Alloy containing **66 % Ni, 31 % Cu and 1.5 % Fe** is completely different from the standpoint of composition (matrix, scale layer) from the highly alloyed steels. The oxidic layer is created by a continuous layer of Ni and Cu oxides (Figure No. 8). The contents of these elements in the oxidic layer correspond with the contents in the matrix. Decreasing of oxygen content by 90% takes place after the reduction and the pickling in non-oxidizing HCL is short. Change of the oxygen content in case of two reducible oxides (NiO, CuO) confirms nearly complete reduction of the oxides. Neither reduced layer, nor the matrix requires pickling in the acid mixtures. Hydrochloric acid is suitable for this purpose. Surface after the pickling in the acid is clean without any residues of oxides.



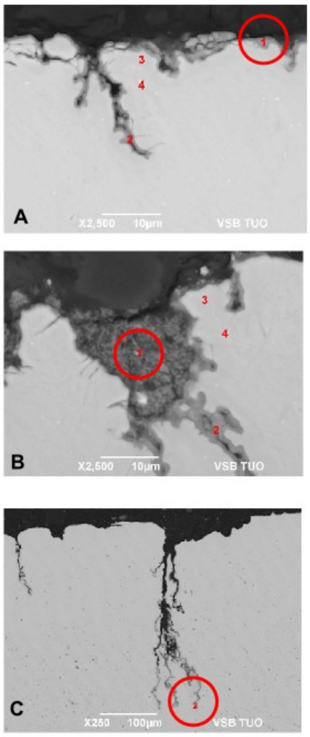


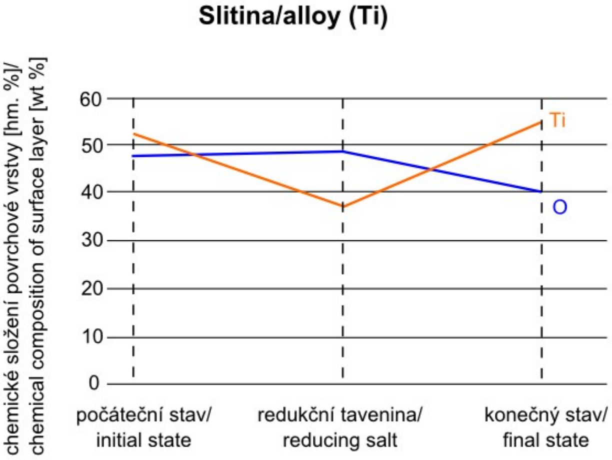
%	—	1,0	31,0	1,5	66,0
	O	**Mn**	**Cu**	**Fe**	**Ni**
A	27,8	0,9	23,8	1,3	46,2
B	0,7	—	14,6	1,7	83,1
C	—	1,0	32,6	1,8	64,6

Obr. 8: Charakter okujové vrstvy slitiny Ni/Cu/Fe a její chemické složení [hm. %] po moření v redukční tavenině a následném domoření v kyselině. A – výchozí stav, B – stav po redukční tavenině (30 min, 0,22-0,32 % NaH), C – stav po domoření v kyselině (HCl).

Figure 8: The character of the scale layer of alloy Ni/Cu/Fe and its chemical composition [wt. %] after pickling in reducing salt and subsequent pickling in acid. A – initial state, B – state after reducing salt (30 min, 0,22-0,32 % NaH), C – state after subsequent acid pickling (HCl).

Titanium is completely different from other tested samples because of its corrosive behaviour (Figure No. 9). The surface is covered by a layer of Ti oxides. Deep inruns into the matrix are visible on the surface, which are also covered by the oxides. Titanium oxides are not reducible by the reducing melt and by pure NaH. But NaOH in the melt reacts with the surface oxidic layer. It ensures its erosion and subsequent short pickling in the mixed acid (HNO_3 + HF) without heating will secure a complete removal of the layer.





%	—	—	—	99,2
	O	Si	Fe	Ti
A	48,5	—	—	51,5
B	49,3	0,6	3,1	37,8
C	40,1	—	—	54,2

Obrázek 9: Charakter okujové vrstvy slitiny Ti a její chemické složení [hm. %] po moření v redukční tavenině a následném domoření v kyselině. A – výchozí stav, B – stav po redukční tavenině (30 min, 0,22-0,32 % NaH), C – stav po domoření v kyselině (HNO3 + HF).

Figure 9: The character of the scale layer of alloy Ti and its chemical composition [wt. %] after pickling in reducing salt and subsequent pickling in acid. A – initial state, B – state after reducing salt (30 min, 0,22-0,32 % NaH), C – state after subsequent acid pickling (HNO3 + HF).

9. Conclusion

Analyses of the oxidic layers and matrix of the wires made from austenitic and ferritic steels, alloys with high content of Ni and metallic Ti were carried out. They confirm data on the mechanism of complete or partial reduction of the scales in the reducing melt. It confirms a suitability of utilization of this way of pre-treatment in 17 pickling plants of austenitic and ferritic steels in the world.

It seems that the utilization of the reducing melt can improve and accelerate pickling, or it can possibly enable an application of pickling acids at lower temperatures and concentrations of the components. This is valid especially for the highly alloyed alloys with Cr, Mo, Ni and Nb that require acids or mixtures with higher concentrations used at higher temperatures and that needs more demanding waste disposal in comparison with the highly alloyed steels. The results support new applications of the reducing melt.

This work is devoted to the memory of Prof. Jiri Mostecky one of the authors of reducing technology invention.

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