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CHEMICAL PREPARATION OF TUBES BEFORE COLD DRAWING

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Review paper

ABSTRACT

Prior to the technological process of cold drawing of tubes through dies, a very important part is preparation for drawing and pre-treatment of tubes. In the production of cold drawn tubes, pre-treatment involves the chemical removing of impurities and oxides, and subsequently applying the lubricant on to the surface of the tubes. For cleaning, pickling, bath of hydrochloric or sulphuric acid is the most commonly used cleaning agent, which is kept at elevated temperatures. This is a significant problem from an environmental point of view, since it is performed at higher temperatures and with chemically aggressive media. This review paper describes the existing procedures for the chemical preparation of niobium microalloyed steel tubes and the ways of reducing the impact on environment, as well as new approaches that are possible alternatives for surface preparation, without the usage of chemically aggressive media.

Keywords: *steel tubes, chemical preparation, cold drawing*

1. INTRODUCTION

Metal forming technology by drawing is a technological process of passing a material through an opening in a die that reduces the cross section and increases the length of the drawn material [1 - 4]. With this technological process wires, rods, different profiles and tubes are produced. Drawing is performed in cold condition at room temperature. In addition to reducing the cross-section, drawing results in better surface quality and greater accuracy in product dimensions. If larger reductions in cross-section are required, then the drawing is performed gradually with more tools (die). The cross-section of the finished product corresponds to the cross-section of the output part of the die in the last run. There are two different basic procedures, figure 1, drawing of full profiles (bars and wires) and drawing of hollow profiles (profiles, tubes).

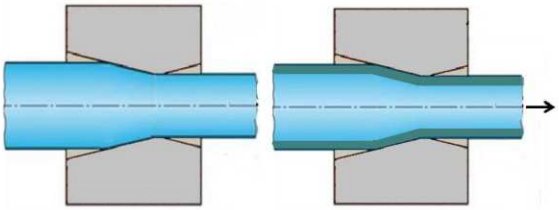

Figure 1. Drawing scheme: a) full profiles, b) hollow profile [1]

Prior to cold drawing, the oxide layer and impurities must be removed from the surface of the semi-finished product (bar or a tube). In order to avoid high friction between the material and the die, the starting tube should be chemically prepared before cold drawing [2 - 5]. This stage of preparation prior to the tube-drawing process is called chemical preparation [2].

Chemical preparation of the tube surface implies a series of complex chemical-technological operations in order to remove all impurities from the tube surface and thus to reduce unwanted friction during cold tube-drawing process. Correctly conducted chemical preparation has a significant impact on the final quality of cold drawn tubes [4, 6, 7]. Different chemical compounds, including acids, are used in this chemical preparation process, which must be handled with care as they can be harmful to both human health and the environment. This refers in particular to acids (sulphuric, hydrochloric, nitric) as well as various soaps, detergents, solvents, etc. [6].

This paper describes the processes performed during the classical chemical preparation of tubes before the technological process of passing through dies, which are still present in production today. An overview is given on the waste products during chemical preparation, as well as on the need for special waste management. The last chapter describes new alternative methods for the preparation of the surface of the tube that are trying to be introduced today in production processes, in order to reduce the environmental impact.

2. CHEMICAL PREPARATION OF TUBES

Chemical preparation of the tube surfaces means a series of complex chemical and technological operations in order to remove impurities from the tube surfaces and thus to reduce unwanted friction during cold tube-drawing process. Properly conducted chemical preparation has a significant impact on the quality of cold drawn tubes [4, 7]. Starting stock for cold drawing can be welded tubes or seamless tubes. These tubes must be previously cleaned with various acids from rust, oxide layers and other harmful substances. Therefore, other processes such as degreasing, rinsing, pickling, phosphating, neutralization are implemented [1].

Chemical preparation consists of the following stages:

- Degreasing,
- Rinsing with hot water,
- Pickling,
- Rinsing (2x cold and 1x hot water),
- Phosphating,

- Rinsing,
- Lubrication.

At the chemical preparation of the tubes, the optimal choice of all parameters achieves the formation of an optimum antifriction layer on the tubes, which is sufficiently adhesive to the surface of the tube, and sufficiently thermally and mechanically resistant, to withstand friction during the cold-drawing process [6].

This layer must be sufficiently resistant, compact and uniform to prevent contact of the tube surface with the die surface, thereby preventing friction and thus excessive wear of the die and better quality of the finished tube surface.

2.1. Degreasing

Degreasing is the first stage of chemical preparation. It is carried out in tubs in soap and detergent solutions. These are surfactants which, by reducing surface tension, emulsifying and dispersing impurities, greatly improve the effectiveness of cleaning the grease from the surface of the tube. As the degreasing agents are used alkaline salts, soaps and/or detergents and emulsions that are mixtures of solvents, soaps, including silicates, phosphates, surfactants [1].

After degreasing, tubes are rinsed in cold water by immersing them repeatedly in tubs. If greasy impurities cannot be eliminated in first step the process is repeated in the dilute sodium hydroxide because metallic soaps can be formed by the reaction of phosphate coatings and alkali soaps. Metallized soaps most commonly occur on tubes that have already been cold-drawn. The tubes are subsequently rinsed in hot water to remove residual grease particles, by repeatedly immersing the tubes in hot water tubs.

2.2. Pickling

Pickling removes oxide layers and rust from the surface of the tubes. It is carried out in tubs with acid solutions, figure 2. In the process, chemical reactions of the oxide layers with acids take place.

Figure 2. Tubs for tube preparation [7]

Stainless steels are pickled in a mixture of hydrochloric acid and nitric acid (2 % HCl + 5 % HNO_3 + 67 % H_2O), at the temperature 40 – 50 °C, from 15 up to 40 min. After pickling, they are rinsed in water and pickled again in 8 % HNO_3. Copper, brass and bronze

are pickled in dilute sulphuric acid. The baths are heated to 60 – 80 °C, so the tub must contain heaters that will heat the liquids and acids, figure 3 [6, 7 - 9].

Figure 3. Tub with heaters [7]

The oxide layer on the steel surface consists of three layers: FeO, Fe_2O_3 i Fe_3O_4, figure 4.

Figure 4. Oxide layer on strip surface [2]

Chemical process of pickling in H_2SO_4:

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$$
$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Chemical process of pickling in HCl:

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$
$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$
$$Fe + 2HCl \rightarrow FeCl + H_2$$

Which reaction will occur depends on the temperature and acid concentration. The pickling time depends on the temperature and the acid concentration, figure 5.

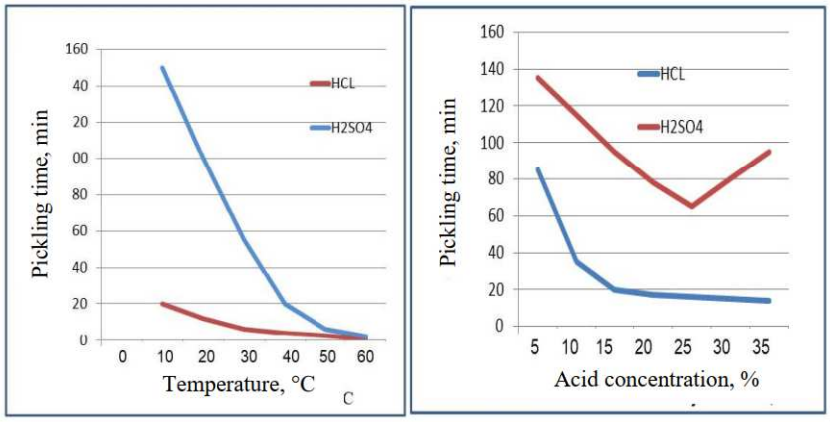

Figure 5. Influence of temperature and acid concentration on pickling time [1, 10]

In reactions of acid with metal, hydrogen is released, which creates pressure between the metal and the oxide layer, resulting in separation and fracture of the oxide layer, figure 6. Pickling is done mechanically by separating the oxide layer from the metal. H_2SO_4 reacts dominantly with metal and HCl dominantly with the oxide layer. Formerly, H_2SO_4 was used more frequently, but as HCl reacts less with metal and accelerates the process of pickling. Regardless of the higher cost HCl is nowadays more commonly used in chemical preparation [11].

a) b)

Figure 6. a) hydrogen penetration to the surface, b) separation of the oxide layer [1]

Hydrogen generated during pickling can penetrate the metal and, with non-metallic inclusions, create bubbles. In addition, it can diffuse into the metal and lead to internal cracks and hydrogen embrittlement of steel.

For this reason the corrosion inhibitors are added to the baths. Inhibitors are organic materials that cause electrochemical reactions and separation on the surface of metals nobler than Fe. Inhibitors are added to prevent the reactions of acids and the base material of the tubes. Depending on the inhibitor used, it is possible to accelerate the removal of the scale from steel and enable the complete removal of all scale from the surface of tubes [12]. Accelerators are added to accelerate the reaction processes of acids and oxide layers (scale). On the surface of the tube a large number of short-circuited local galvanic microelements are formed. Additionally, by adding inhibitors the surface layer is created that prevents hydrogen from penetrating in to the steel.

Since acid treatment is hazardous and environmentally unfavourable, disposal of used acid is also environmentally unfavourable, where possible pickling is replaced by other methods for removal of the oxide layer. Today, pickling is carried out on semi-finished products before cold drawing process and before the protection of finished products by galvanization. After pickling prior to cold drawing, the tubes are two times thoroughly rinsed

with water. First time with cold flowing water in the baths by repeatedly immersing the tubes in the baths, and second time in warm water, followed by drying of the tubes [6-9].

2.3. Phosphating

The phosphating process is carried out in steel tubs. Tubs are lined with thin sheet of alloy steel preventing the sludge, formed during operation, from settling on the walls of the tub. Phosphating of tubes is carried out by immersing the tubes in a solution of zinc phosphate, operating at temperatures less or equal to 82 °C. During this process, a crystalline film of phosphate coating is formed on the tubes surface. During cold deformation, this film acts as a carrier for lubricant, enabling a firm adhesion between the lubricant and the surface of the tube. This improves lubrication, increases the drawing speed of tubes, extends tool life and reduces the possibility of pressure welding between tube and tool. Traces of acid that are left behind on the surface of phosphatized tubes are needed to be well rinsed in cold water [7].

2.4. Lubrication

The final stage of chemical preparation is lubrication, which allows the formation of an antifriction layer that is sufficiently adhesive to the surface of the tube, and sufficiently mechanical and heat resistant to withstand the friction that occurs when the tube is passed through the die. Lubrication is carried out in a bath with alkaline solutions, e.g. sodium soap. It is necessary to heat the bath up to 70 °C for better adhesion of the soap and for faster drying of the tube on the air.

3. ALTERNATIVE PROCEDURES FOR CLEANING THE SURFACE OF STEEL PRODUCTS

In the picking process of steel pipes, a certain amount of by-products are produced. These by-products include significant amounts of wastewater with increased acidity due to acid residues. In the tubs for pickling and flushing of the tubes, there is a precipitation of the iron chlorides and other various metal salts resulting from reaction between the acid and metals. It is thought that when acids concentration drop below 75 % - 85 %, the replacement of acid is required as the pickling process slows down [12 - 14].

Over time, the concentration of metals in the acids also increases in the range of 150 - 250 g/dm^3, which decreases the efficiency of the acid in the metal cleaning process [12 - 14]. According to the Waste Catalog Regulations, this waste is classified as hazardous industrial waste [15]. Waste management and / or acid regeneration are expensive processes. For this reason, the need to find new procedures for the chemical preparation of pipes has been imposed.

Methods for mechanically removing scale and oxide layers from the surface of steel such as brushing shot blasting, etc. are already known [16 - 17]. However, these procedures could not produce the same clean surface as the pickling process, and scratch marks from cleaning are often visible on the surface of products. New efforts are being made to investigate combinations of multiple mechanical methods that could completely clean the steel surface. One way to prepare the surface is certainly a combination of bending and brushing [18]. By this process, the oxide layer is subjected to tensile and compressive loads

when bending over the rollers, which results in the separation of the scale from the steel. This is followed by brushing to remove most of the residual oxides and scales.

Another method today in use is Smooth Clean Surface (SCS) [19, 20]. It is a process that seeks to reduce or completely prevent the formation of scales and oxides during steel production. The procedure is applied during the hot rolling of steel. The process is based on the mechanical cleaning of the steel surface; the steel pieces are passed through sets of rollers that have brushes on them. Three sets of such rollers are frequently used, which are constantly supplied with recirculating water to flush out the scale. The upper layers of hematite and magnetite and part of the inner layer of wüstite are removed in this way. Residual wüstite is considered to be a barrier for further corrosion of steel. Although environmentally friendly, this process does not remove all scale and leaves a slightly rougher surface in comparison to pickling. Therefore, it is often used in combination with Eco-Pickles Surface (EPS) method.

The EPS process comes down to the cleaning of the steel surface with a jet of water containing the abrasive agent. EPS is a new method of cleaning the surface of the steel that is completely environmentally friendly. According to research, quality of the surfaces can completely replace chemical cleaning [21]. The EPS process at the first stage brakes mechanically scales on the surface of steel by passing it between hardened rollers. After this steel enters the "EPS slurry blasting cell", that has water with abrasives in it, and blasts the surface of the steel in the form of slurry jet at high velocity [20, 21]. This cleans surface of all impurities and oxides formed in the previous methods of processing. According to experience from the facilities in which this procedure is used, it is obtained a clean steel surface which in some cases is even better than that obtained by chemical preparation.

Today, the most acceptable procedure for removing the oxide layer from hot-rolled tubes is a descaling process, consisting of spraying a hot steel surface with water and passing the product through a pair of rollers. The cooled down oxide layer become fragile, breaks down by passing through the rollers and after it is washed with water. In this way, a considerable part of the oxide layer is removed from the outer surface. Subsequent chemical preparation results in significantly less environmentally-unfriendly by-products and the need for acid regeneration is reduced.

4. CONCLUSION

Chemical preparation (pickling) is a very important stage of preparation in technology for the production of cold-drawn tubes. The quality of the chemical preparation does not only influence the surface quality of the finished product. Poor chemical preparation can also affect the dimensions of finished tubes and in some cases it can affect the other tube properties. The economic aspect is also important because the poor chemical preparation increases the tool wear and damage of dies for cold-drawing.

The paper describes the chemical preparation (or pickling) of the tubes that is most represented in the technologies for the production of cold-drawn tubes.

Today, mainly for environmental reasons, new surface preparation processes are being developed. Increasingly stringent regulations seek to reduce the amount of used chemicals. The greatest interest is in procedures such as SCS and EPS. Their development has not yet reached the desired level so that they can replace the described chemical preparation. In technology for the production of cold-drawn tubes, EPS is a more acceptable method, but only in the process of cold-drawing in which the mandrel is not in use.

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