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Pickling of Stainless Steels—A Review

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ILLUSTRATION

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/ft^2	ampere per square foot	μm/yr	micrometer per year
°C	degree Celsius	rpm	revolution per minute
min	minute	vol pct	volume percent
μm	micrometer	wt pct	weight percent

PICKLING OF STAINLESS STEELS–A REVIEW

By Bernard S. Covino, Jr.,[1] John V. Scalera,[1] and Philip M. Fabis[2]

ABSTRACT

The Bureau of Mines is conducting a study of methods to improve the efficiency of the process used to pickle stainless steels. A review of the literature on pickling of stainless steels showed that the chemistry of several process operations involved in the pickling of stainless steels is not fully understood, and that further research could improve the pickling efficiency. The benefits of this research would be a reduction in the annual loss of several thousands of tons of critical minerals such as nickel and chromium, and a reduction in the amount of solids and spent acid solution that are currently discarded. The conclusion from this review is that further research is needed in four operations that either directly or indirectly influence the pickling process: hot working, annealing, conditioning, and the actual operation of pickling. Laboratory studies of the pickling operation are presently in progress.

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INTRODUCTION

The various operations involved in processing stainless steels are given in figure 1. After being worked by hot or cold rolling, the steel is softened by annealing. Oxide forms on the stainless steels during this annealing process, which, as shown in figure 1, occurs several times. Conditioning is used to facilitate the pickling process. Mixed-acid pickling, or pickling by a solution of two or more acids, is then used for cleaning the oxide-covered stainless steels. In addition to removing the annealing scale, pickling also removes a very thin (1- to 5-μm) region depleted in chromium between the oxide and the bulk stainless steel. Loss of chromium and nickel from this region and the oxide is inherent in this part of the pickling operation. In practice, the stainless steel may be left in the pickling solution longer than necessary, causing excessive dissolution of the bulk steel, resulting in losses of several thousand tons of chromium and nickel annually. The combined dissolution products can build up to a point where the action at the pickling bath stops, resulting in a sizable disposal problem when the bath is replaced. The dissolved metals also increase the use of acids in the pickling bath by complexing or precipitating acid salts. The need to study the pickling process was formulated during discussions between the Bureau of Mines and the American Iron and Steel Institute (AISI). Both groups concluded that the problems of loss of critical minerals, excess use of acids, and disposal of spent solutions could be lessened by a better understanding of the entire pickling process.

The literature pertinent to the pickling of austenitic stainless steels was reviewed. Data bases such as Chemical Abstracts, Metadex, Compendex, and NTIS (National Technical Information Service) were searched from 1900 to 1983 where applicable. Although articles in all languages were accepted in the search, the review was done mainly on articles in English. The general purpose of the review was to assess the technology of stainless steel pickling and to present a critical examination of the mechanism of mixed-acid pickling of stainless steels in terms of all the important process operations and operating parameters.

All such operations and parameters are considered in light of how much knowledge is available and what further knowledge is necessary for a better understanding and control of the pickling process. This review begins by considering those factors in the metal-forming operation that can affect subsequent pickling behavior. The effect of annealing on pickling is then addressed. Conditioning treatments prior to pickling have a very

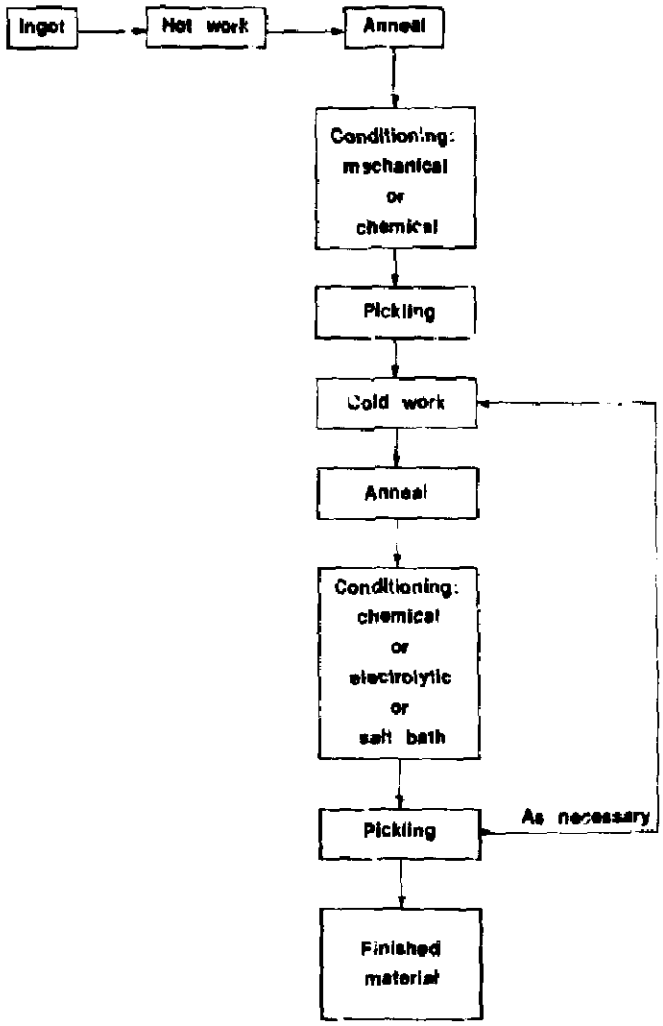

FIGURE 1. - Schematic of steps involved in processing stainless steels. Indicated steps are repeated as often as necessary to thin the material to the desired thickness.

significant effect on pickling and are addressed next. Finally, the operation of the pickling bath is considered. The present understanding of the mechanism of pickling of stainless steel is developed in detail in this last section.

EFFECT OF HOT AND COLD WORKING ON PICKLING

In order to be inclusive, the effects of hot and cold working on the pickling of stainless steels are briefly considered. Working of the stainless steel usually has no direct effect on the pickling operation because an annealing operation is interposed between the working and the pickling steps. However, some effects of hot and cold working can influence the annealing operation or remain unchanged after the annealing operation. Of the two types of working, hot working presents the greatest potential problem because of its ability to change the chemistry and grain structure of the stainless steel, resulting in subsequent changes in the scale formed during annealing.

HOT WORKING

Hot working, the process of mechanical deformation of a material at temperatures above its recrystallization temperature, can significantly alter the grain size of metals. The degree to which this alteration occurs for alloys such as stainless steels depends on the degree of deformation, the number and frequency of deformation steps, and the initial and final working temperatures. The degree of deformation determines the stored energy in a material that is the driving force for recrystallization to occur. The frequency of deformation steps and initial and final temperatures determines the rate of crystallization and the occurrence and rate of grain growth. Both a lower deformation temperature and a greater amount of deformation produce a smaller ultimate grain size. It is usually the temperature at which hot working is completed, the finishing temperature, that determines the average grain size (1).[3]

When hot working operations are followed by an anneal, the major effect of this altered grain size is on the resulting annealing scale. If the mill scale conforms to the morphology of the metal surface, then a fine-grained scale forms on a fine-grained metal and a larger grained scale forms on a large-grained metal. Recent research (2) has shown that the scale formed on smaller-grain-size stainless steels contains more chromium than that on larger-grain-size steels. Oxide films containing more chromium could significantly affect the rate of pickling and possibly cause compositional changes, such as chromium depletion, in the metal adjacent to the oxide.

Severe problems can occur after hot working if there is significant chemical inhomogeneity or large quantities of inclusions in the initial ingot. Regions of the ingot depleted of an alloy constituent could be smeared in the rolling direction, resulting in bands of different composition (3). Another phenomenon, similar in appearance to banding, is fiber. This elongated structure consists of nonmetallic inclusions which are elongated as the steel is worked (4). While the spontaneous recrystallization that occurs during hot working is usually unable to affect these localized composition changes, annealing usually eliminates them. If these variations in metal composition are still present after the annealing step, however, preferential attack of the banded regions or pitting near the fibers could result in an irregular surface morphology. Since stainless steel chemistry is closely controlled, these structures are rarely seen in commercial stainless steels; if present, they would be expected to significantly affect the pickling process.

Sensitization to intergranular corrosion may occur in austenitic stainless

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

steels when they are subjected to a working temperature range of 450° to 900° C or when the steel is slow-cooled from 1,050° C (5). A chromium-depletion theory proposes that the precipitation of $M_{23}C_6$ carbides along a grain boundary results in a region depleted of chromium adjacent to the carbides. In some cases of very high purity (low-carbon) alloys, although there is no detectable carbide precipitation, a solute segregation theory proposes that a chromium-depleted region still exists (6). The resistance to the pickling solution is greatly reduced in these regions. Essentially, two dissimilar metals are in contact and an unfavorable anode-cathode area ratio is present (7, pp. 35-36). In this case, the depleted zone sets up active-passive cells with large-area alloy grains acting as cathodes in contact with material in the grain boundaries of limited area acting as anodes. In addition, the grain boundary carbides can be susceptible to the mixed acid solution, and their dissolution would produce further surface degradation. As with the banding and fiber phenomena, however, any sensitization should be removed in a proper annealing step, making hot-work-induced sensitization a minor problem area.

COLD WORKING

Cold working increases the stored energy of a material and, when coupled with an annealing process, can cause grain size changes similar to those discussed for hot working. But, unless a deformation-induced segregation or transformation occurs that brings dissimilar concentrations of atoms into contact (8), cold working has no other effect on the pickling behavior of properly annealed stainless steels. Simultaneous deformation and pickling never occur in the industrial processing scheme of stainless steels; therefore, cold working is important only if new phases or the segregation of alloyed components result from the plastic deformation.

EFFECT OF ANNEALING ON PICKLING

Compared to hot and cold working, annealing probably has a more significant effect on the pickling rate of stainless steels than any other process preceding pickling. Annealing can be thought of as a relatively uncontrolled oxidation reaction; that is, the temperature can be controlled fairly accurately, but the atmosphere within the annealing furnace is usually not controlled. Also, from batch to batch of stainless steels, the heat-up time, time at temperature, and cool-down time are different for various metallurgical reasons. This variability in the annealing process can have a significant effect on the mill scale formed and thus on the ease of pickling of the stainless steel. Numerous investigations concerning the high-temperature oxidation of stainless steels in various atmospheres are available throughout the metallurgical literature. Although there is considerable disagreement about the structure, thickness, and growth mechanisms of the films, some agreement concerning film characteristics exists.

Because of the short annealing times involved in stainless steel processing, the gaseous annealing environment reacts preferentially with the more reactive chromium component. This produces a region of the base metal near the oxide that is significantly depleted in chromium. Consequently, the thin oxide films that form on these alloys during the initial oxidation stages are composed mainly of Cr_2O_3 with small amounts of Fe_2O_3 or a spinel phase $FeFe_{(2-x)}Cr_xO_4$ where $0<x<2$ (9-12). These films are fairly adherent and protective, and since their ionic conductivity is low (13), they prevent diffusive penetration of other ions and atoms through the scale. Although the Cr_2O_3 films are adequate barriers, the iron oxide films are quite permeable, especially to carbon (14). Under conditions of severe scaling, a stratified structure occurs that contains Cr_2O_3, $FeFe_{(2-x)}Cr_xO_4$, FeO, Fe_3O_4, and Fe_2O_3 (8, 15). In certain cases, as in extended heating periods, the initially protective scales then become nonprotective.

The scaling behavior of stainless steels under conditions similar to those in annealing furnaces has not been adequately studied. Brief exposures (1- to 5-min time at temperature) in complex (O_2, H_2O, CO, CO_2) high-temperature (871° to 1,038° C) environments should be studied. Complete characterization of the scales resulting from these exposures must be done in order to understand the chemistry and structure of the complex scales formed on stainless steels. It would then be necessary to correlate the ease of pickling of the steels with the chemistry and structure of the annealing scales, an area of research that could have significant impact on the pickling process as currently used.

Because of the elevated-temperature anneal, three other metal-related phenomena that could have an impact on subsequent pickling operations are embrittlement, sensitization, and a transformation to a dual-phase structure.

Embrittlement (1) may occur upon heating or slowly cooling certain ferritic and high-nickel austenitic steels through the 425° to 760° C temperature range. A precipitation reaction occurs in this temperature range producing a complex structure FeCr phase, the sigma (σ) phase. Because this phase is rich in chromium, the presence of a chromium concentration gradient between the σ-phase and adjoining phases may affect the pickling behavior and corrosion resistance of stainless alloys (8). With proper temperature control, however, this phase will not form.

Elemental concentration gradients arise in the alloy owing to diffusional processes at elevated temperatures. For instance, if an 18Cr-8Ni stainless steel (i.e., 304) is heated to 1,150° C (a common heat-treatment temperature) and water-quenched, the single-phase austenitic alloy is formed. The quenched-in austenitic structure is thermodynamically unstable at room temperature, but the transformation kinetics are extremely slow. If the same alloy, assuming a low carbon concentration, is heated to 1,200° C and allowed to soak at that temperature for several hours, the FCC austenite partially transforms to ferrite, a BCC structure. Therefore, a two-phase (austenite-ferrite) microstructure can be present. A problem arises in that the austenite phase contains more nickel and less chromium relative to the ferrite phase (8). Thus, an elemental concentration gradient is created between adjacent grains. The susceptibility of the alloy in this condition to localized corrosion in a mixed-acid pickling bath may be significantly enhanced. This enhancement is attributable to a galvanic effect arising between grains of different composition in close proximity.

The final problem produced by elevated-temperature exposure of stainless steels is sensitization. Depending upon the carbon content of the alloy, precautions may have to be taken to avoid sensitizing conditions during annealing. As mentioned previously, sensitization results in intergranular precipitation of $M_{23}C_6$ carbides of high chromium content and chromium depletion of regions adjacent to these grain boundaries to below the necessary 12 wt pct required for stable passivity (7, pp. 35-36). While this would cause an increased localized attack, sensitization is rarely a problem in the production of austenitic stainless steel.

In summary, hot working and, to a small degree, cold working can have potentially deleterious effects on the pickling of stainless steels. Grain-size variations can cause variations in scale chemistry, and ingot inhomogeneity can cause banding and fibering. Sensitization can occur in both hot working and annealing, but embrittlement usually occurs only during annealing. Typical annealing processes are poorly controlled, resulting in variations in scale chemistry. All of these problems do not necessarily occur during present-day stainless steel processing, but there is a very real possibility for their occurrence. Therefore, in order to fully understand the pickling process and everything that affects it, the more important of these problems (grain-size variations and annealing variations) should be studied further.

EFFECT OF CONDITIONING ON PICKLING

Conditioning of stainless steels is a process used to prepare annealed stainless steel for the pickling process. Its purpose is to alter the annealing scale in order to reduce the time, temperature, and acid concentration used in the pickling process. The scale is either cracked by thermal or mechanical means, or constituents in the scale are chemically or electrolytically altered to increase their solubility in order to be able to reduce either the amount of HNO_3 and HF in the final pickling solution or the times and temperatures in the pickling process.

In contrast to the well-understood mechanical conditioning process, the chemical and electrolytic conditioning techniques need to be studied further in order to understand exactly what chemical and structural changes result from the respective technique.

DEGREASING

Although degreasing is usually done before annealing stainless steels, it also may be necessary, prior to a conditioning step, to remove surface contaminants such as oil, grit, graphite, metal chips, or other foreign matter that may have been transferred to the steel surface. Depending on the type of foreign matter suspected on the surface of the steel, various techniques are employed. These techniques include the use of vapor degreasing with organic solvents, water-soluble emulsifiers, chelates, and water-soluble alkaline cleaners (16). Contaminants on the surface of the heat-treated steel can often result in an oxidized grime during scale conditioning, which can severely inhibit the effectiveness of the subsequent pickling processes. Surface contamination also pollutes the pickling solutions, which reduces their effectiveness.

Once the surface has been effectively cleaned, conditioning techniques help to oxidize, crack, and loosen scale to enhance the effectiveness of final pickling operations. Depending upon the nature of the oxide film, various techniques are employed. Both mechanical and chemical techniques have been used successfully. The basic mechanical technique for scale conditioning is abrasive blasting.

ABRASIVE BLASTING

Abrasive blasting is one of the fastest of all conditioning techniques and has been successfully used in both batch and continuous on-line processing of stainless steel strip (16-18), although it is used almost exclusively on the latter. Abrasive blasting uses steel shot or silica in sizes ranging from 100 to 2,500 mesh depending on the material being conditioned. The abrasive is either dropped or directed by air pressure toward the surface of the steel at angles and velocities that allow the cracking, loosening, and partial removal of heavy oxide scales without cold-working the steel's surface. The technique has limited application for batch-processing complex shapes because some oxidized areas not exposed to the shot blast are not totally conditioned. The use of carbon steel shot as an abrasive has been a topic of controversy (19). Opponents feel that its use can embed iron particles in the surface of the stainless steel, resulting in future corrosion problems. This would, of course, depend on what treatments followed the carbon steel blasting. The abrasive silica used in blasting must be low in iron in order to avoid surface contamination. As with most mechanical descaling techniques, caution must be practiced to avoid work-hardening the steel surface. Heat-treated surfaces with thin oxide films, such as cold-rolled products, are usually not conditioned using mechanical techniques.

CHEMICAL CONDITIONING

The choice of chemical conditioning parameters varies significantly between stainless steel processing plants. Some of the parameters that must be taken into consideration are the nature of the base

metal and oxide being removed, strip or batch processing, and chemical costs. For example, when working with an intermediate pickled 304 stainless steel, some companies use a salt bath conditioning process followed by an electrolytic nitric acid bath before the final HNO_3-HF acid pickle; other processors go directly from the salt bath into the final pickling bath. The following paragraphs describe some of the more common chemical conditioning processes in use.

Reducing Acids

Reducing acid baths descale a metal by reducing the oxides in the scale and also liberate hydrogen at the oxide-metal interface. The most common reducing acids used in conditioning processes for annealed stainless steels are H_2SO_4 and HCl. The specific acid solution used depends on the nature of the base material and oxide being treated; chemical costs, as well as the time permitted for conditioning, are usually determined by whether the metal is prepared by either continuous strip or batch processing. Solutions of 10 to 15 vol pct H_2SO_4 at 60° to 71° C are used for conditioning heavy oxides (20). H_2SO_4 solutions are relatively slow in comparison to solutions combining H_2SO_4 (6 to 10 vol pct) with HCl (6 to 10 vol pct) at 54° to 60° C (21, pp. 684-689). Although HCl is not as aggressive as H_2SO_4 in attacking the base metal at elevated temperatures (77° to 93° C), it is much more aggressive in attacking iron oxides than is H_2SO_4. The use of conditioning solutions containing HCl requires critical control because ferric chlorides formed during the conditioning process can result in pitting of the base material (19). Another conditioning solution that can cause base metal pitting is H_2SO_4 (8 to 11 wt pct) combined with NaCl (5 to 6 wt pct) at 60° to 65° C (18).

Oxidizing Acids

In contrast to reducing acids, oxidizing acids descale by oxidizing the scale to a higher oxidation state, thus increasing the solubility of the scale. HNO_3 (8 to 10 vol pct at 38° to 54° C) is the most commonly used oxidizing acid (19). Because of the greater cost of HNO_3 compared to H_2SO_4, however, its use has been limited in the conditioning processes.

ELECTROLYTIC ACID CONDITIONING

Experimental studies on electrolytic pickling in acid solutions were described by Tamba, Azzerri, Bombara, and others (22-25). Industrial electrolytic conditioning using an H_2SO_4 bath can be traced back to the 1920's and 1930's where there was a need for faster pickling techniques to maximize output from on-line stainless steel strip processing (26).

The most common acids associated with electrolytic conditioning are H_2SO_4 and HNO_3. Electrolytic acid conditioning techniques are used presently on both martensitic and ferritic steels which, during the annealing process, have developed tightly adhering thin oxide films (21, pp. 689-690). Austenitic chromium-nickel steels can also be electrolytically conditioned, although this conditioning requires caution because of the greater potential for surface pitting. The probability of pitting is increased for thicker oxide scales because breaks in the oxide scale react more rapidly than scale-covered base metal. This highly localized activity can result in pitting before the bulk of the scale is removed.

Anodic Conditioning

There are three basic types of electrolytic conditioning: anodic, cathodic, and alternating current (27). Anodic conditioning either electrically oxidizes (dissolves) the surface or forces the surface into a passive state by an applied anodic potential. When the surface is being electrically oxidized, the base metal is being attacked and the scale dislodges. When the surface is passive, then the base metal undergoes far less attack than the oxide scale, releasing oxygen gas at its surface. The oxygen mechanically agitates the solution,

uplifts the surface scale, and can oxidize contaminants such as organic impurities. An example of an anodic electrolytic solution is 2 pct HNO_3 used at a current density of 75 to 200 A/ft^2 (21, pp. 689-690; 27).

Cathodic Conditioning

During cathodic electrolysis, the workpiece is charged to act as a cathode. The base metal is electrochemically protected while the oxide scale is being reduced. Cathodic electrolysis is faster than anodic; hydrogen gas generated on the metal surface helps to agitate the solution and lift off the oxides. In martensitic steels, however, this reaction can result in hydrogen embrittlement of the surface (27-28).

Alternating Current Conditioning

Very low frequency (one cycle per several minutes) alternating current electrolysis is used in conjunction with stainless strip processing where direct electrical contact to the workpiece is difficult. In fact, the current is usually reversed only from tank to tank in a two-tank method, or, in a one-tank method, it is reversed once in the tank. The basic reactions, however, are the same as described in anodic and cathodic conditioning. Operationally, the electrodes are placed above and below the strip, forming an anodic potential on one side of the strip and a cathodic potential on the other side (27). During each alternating cycle, the polarity is reversed on the electrodes and, in turn, on the faces of the stainless steel strip. A variation is the use of two tanks where the strip in the first tank is made cathodic with respect to the anodic electrode in the tank (26). Here the base metal is electrochemically protected and hydrogen gas is formed to lift off the oxides. The strip then enters a second tank where it becomes anodic with respect to the cathodic electrode placed in the second tank. Here the surface and scale are oxidized and release oxygen at the surface, which uplifts the scale. An example of an alternating current electrolysis solution is 10 vol pct H_2SO_4 used at 88° C with a current density of 100 to 150 A/ft^2 (27).

Both ferritic and martensitic steels undergo annealing processes which form thin, tightly "skinned" oxides. Removal of these oxides by mechanical means could cold-work the surface. However, the use of reducing acids, such as H_2SO_4, which release hydrogen during the alternating current descaling process when the workpiece is the cathode, can be detrimental to martensitic steels. As in cathodic conditioning, these steels are subject to hydrogen embrittlement. Alternative conditioning techniques for martensitic steels include those in which the liberation of hydrogen on the steel surface is eliminated.

ELECTROLYTIC NEUTRAL CONDITIONING

Electrolytic neutral (the Ruthner "Neolyte" process) conditioning is similar in mechanical design to electrolytic acid conditioning in that alternating cathodic and anodic electrodes are used to polarize the workpiece and induce oxidation and reduction of the surface scale (29). The electrolytic neutral pickling involves a Na_2SO_4 solution at temperatures of 65° to 85° C, resulting in safer operation conditions and reduced energy costs (29). The final stages in the process result in a regeneration of the Na_2SO_4.

SALT BATH CONDITIONING

The use of both aqueous and molten salt baths as a pretreatment for acid pickling has been successful in increasing the ease of scale removal of all stainless steel types, permitting the use of reduced acid concentration and decreasing the time of pickling needed to remove the scale (16, 19, 30-31). This reduction in acid concentration and pickling time reduces the likelihood of hydrogen embrittlement in susceptible alloys. Other benefits of salt bath descaling are its fast process time and uniform surface finish (19).

Salt bath treatments can be either reducing, oxidizing, or electrolytic (16, 30). Reducing and electrolytic baths have proven to be more effective in attacking heavy, tightly adhering oxide scales.

Reducing Bath

Reducing salt baths consist of a molten bath of NaOH (371° ± 11° C), containing 1.5 to 2.0 wt pct sodium hydride (16, 30). The sodium hydride is formed in generators along the side of the descaling tank. Sodium and hydrogen gas react to produce the hydride, which must be constantly generated since the level of sodium hydride in solution is depleted during descaling. There are safety hazards involved in the use of sodium and hydrogen. Descaling takes place as the oxide films are reduced to a lower oxidation state:

$$M_2O_3 + xNaH = xNaOH + M_2O_{3-x}.$$

After the workpiece is removed from the salt bath, it is water-quenched. This quenching thermally shocks the remaining oxide layer, fracturing and loosening it and making it more susceptible to the acid pickling.

Oxidizing Bath

As with the previously described caustic reducing salt bath, oxidizing salt baths also use molten NaOH (60 to 90 wt pct) at elevated temperatures (482° C) (16, 30). Other constituents include sodium nitrate (7 to 32 wt pct) and sodium chloride (1.5 to 6 wt pct). Some of the oxidizing reactions that take place are (31)--

$$2FeO + NaNO_3 = Fe_2O_3 + NaNO_2$$

$$Cr_2O_3 + 3NaNO_3 = Cr_2O_6 + 3NaNO_2$$

$$2NiO + NaNO_3 = Ni_2O_3 + NaNO_2$$

$$C + 2NaNO_3 = CO_2 + 2NaNO_2$$

As long as the bath is in contact with air, the $NaNO_3$ can be regenerated by the oxidation of the $NaNO_2$ formed. Trivalent chromium is oxidized to the hexavalent state, which readily dissolves into acid pickling solutions.

Upon leaving the salt bath, the workpiece is quenched with water. The thermal shock involved in quenching the workpiece disrupts the oxidized scale. After the water quench, an acid pickling bath is needed to dissolve any remaining oxide.

An aqueous oxidizing salt bath consists of NaOH (20 wt pct) and $KMnO_4$ (5 wt pct) (32). This strong oxidizing solution may be used on all grades of stainless steel, especially where a light, tightly adhering scale has formed, such as is the case in cold rolling or in some controlled annealing atmospheres. The $KMnO_4$-NaOH solution may also be used on heavier oxide scales. As with the other previously mentioned molten salt baths, the treatment is followed by acid pickling.

Electrolytic Bath

The use of an electrolytic technique in combination with molten salt baths has been applied successfully to continuous stainless steel strip processing lines. A typical bath consists of 75 pct NaOH, 10 pct NaCl-NaF, 14 pct Na_2CO_3, and 1 pct other carbonates and is operated at 482° C. The salt baths are neither oxidizing nor reducing in nature until electrically polarized. Polarization of the workpiece is achieved by the use of a series of cathodes followed by anodes in the neutral salt bath (16, 30). Opposite the cathode, the strip acts as an anode with oxidation taking place. As some of the scale is dissolved into solution, it reacts with the oxygen released during the oxidation process to form insoluble hydroxides. These hydroxides will not interfere with the surface of the steel strip as it becomes cathodic and undergoes reduction. The strip becomes cathodic as it passes below the anode. As reduction takes place at the scale-surface interface, hydrogen evolves, lifting the scale off the surface. After the sample passes through the salt bath, it is water-rinsed and acid-pickled for final scale removal and surface finish.

EFFECT OF PICKLING BATH VARIABLES ON PICKLING

The pickling of stainless steels requires three distinct processes. The first process is the removal of the thermally grown oxide scale for appearance purposes and to facilitate further cold working of the steel. The second process maximizes the corrosion resistance of the final steel product by completely dissolving the chromium-depleted zone that is generally formed during short high-temperature anneals in oxidizing environments. The third process dissolves the minimum amount of bulk steel necessary to give the desired whitening effect. These three processes occur, to some degree, simultaneously during the pickling operation and most probably are interdependent. Therefore, to understand the pickling operation, it is necessary to understand the effect of pickling bath variables, solution composition, and temperature on the pickling operation as a whole and on the dissolution of both the chromium-depleted region and the bulk steel.

PICKLING OPERATION

Before considering the effect of bath variables on the pickling of stainless steels, it is necessary to assess the state of understanding of the mechanism of pickling. It is generally agreed in the literature (24) that the pickling of stainless steels is accomplished by undercutting the oxide and that the high chemical reactivity of the chromium-depleted zone essentially controls the rate of the pickling operation. There were, however, no in-depth studies of the mechanism or even any proof found in the body of literature reviewed here. While it was difficult to determine how this mechanism was discovered, it is clear that little is known empirically about the mixed acid pickling of stainless steels. Other research indicates that dissolution of the oxide is inconsequential in the actual removal of the oxide (23). What appears to be important is that the oxide be sufficiently disrupted to permit the penetration of the pickling solution. Most changes in oxide porosity occur during the conditioning process.

The ideal pickling solution is one that will easily penetrate the thermally grown oxide, rapidly dissolve the chromium-depleted zone, and dissolve only a small layer of the bulk steel. This solution would optimize the rate of pickling while minimizing the unnecessary and excessive loss of bulk alloy. The most commonly used pickling solution for austenitic stainless steels is a mixed acid consisting of HNO_3 and HF in various proportions. By varying the ratio of HNO_3 to HF, it is possible to pickle different types of austenitic steels. This solution accomplishes all three processes listed above and provides a very white surface. There are, however, potential problems of overpickling the steel, resulting in excessive grain boundary attack. This could affect the reflectivity of the surface and decrease the corrosion resistance. This mixed acid is also expensive and extremely dangerous. A possible alternative to HNO_3-HF pickling was reported in a series of research articles (22-25). This research resulted in a technique (24) that used an applied potential to dissolve the chromium-depleted zone while minimizing the dissolution of the base material in an H_2SO_4 bath. The researchers claim that a proper choice of potential can optimize the pickling of stainless steels while using the less hazardous H_2SO_4 solution. However, this technique does not produce as reflective a surface as produced in free (not potential controlled) pickling in HNO_3-HF mixtures. The researchers also did not investigate the effects of iron, chromium, and nickel buildup in the bath on the potential controlled pickling or the quality of the pickled surface. As in HNO_3-HF solutions, these impurities could affect the electrochemical reactions and the rate of pickling, and could even lead to pitting or increased intergranular attack.

Other pickling solutions have been examined in previous research efforts. In one study (33) the solutions were selected for their ability to dissolve the bulk steel. This research reported on the relationship of the composition of the pickling bath to the dissolution rate of 304 stainless steel. Using various combinations of H_2SO_4, HCl, HNO_3, and $NaNO_3$, it was shown that HCl and HNO_3 have about an equal effect on the dissolution rate of scale-free 304 SS, while H_2SO_4 has a much lower effect and $NaNO_3$ has a much greater effect ($NaNO_3$>HCl=HNO_3>H_2SO_4). The results of this study assumed that each chemical in the pickling bath can operate individually with no synergistic effect. However, the same group of chemicals produced different results on annealed and oxide-covered 304 stainless steel. The $NaNO_3$ solution had the slowest pickling rate, while HCl had the fastest pickling rate. Both H_2SO_4 and HNO_3 had intermediate rates. This suggests that while dissolution may be important in the mechanism of pickling, dissolution of the bulk alloy may not be critical. When solutions containing HF were tested, results showed that it had as strong an effect on pickling rate as HCl. HCl is usually not used because the $FeCl_3$ formed generally promotes pitting of the stainless steel. No studies of the effect of temperature on the pickling of stainless steels were found in this search of the literature.

BULK ALLOY DISSOLUTION

Solution Composition

The aforementioned report (33) suggested that dissolution of the bulk steel may not be critical in determining the rate of pickling of stainless steels. The dissolution rate of the bulk steel does, however, control the amount of bulk steel lost to the pickling solution and to some extent the amount of dissolved metal species in solution. The factors that could affect this dissolution rate are temperature, acid concentration, dissolved metal concentration, and agitation. Since many dissolution reactions exhibit some dependence on convection and diffusion, agitation of the solution should be important. A study (34) was done that showed that agitation, as simulated by a rotating disk electrode, significantly affects the dissolution of a 304-type stainless steel (Kh18N10T) in HNO_3 + NaCl solutions. Dissolution rates for samples rotated at 0 to 300 rpm were not affected, whereas rates increased steadily with increasing rotation speed from 300 to 10,000 rpm. The investigator assumed that the agitation affected mainly the cathodic reduction of nitric to nitrous acid, but offers no evidence. Another investigator has shown (35), to the contrary, that the anodic reaction of nitric acid on platinum is diffusion dependent while the cathodic reaction is only reaction dependent.

Acid Concentration

The effect of HNO_3 concentration on the dissolution of austenitic stainless steels is minimal over a range of concentrations and temperatures that would be used in pickling solutions. Isocorrosion diagrams (7, p. 243) for 18-8S[4] steels show that the corrosion rate ranges from 0 to 125 μm/yr for HNO_3 concentrations up to 50 wt pct from 30° C to the boiling point. The dissolution behavior of several of the more popular austenitic stainless steels and of some iron-chromium-nickel alloys has been thoroughly reviewed (36) elsewhere. The results simply show that HNO_3 solutions (<50 pct) do not rapidly dissolve austenitic stainless steels.

Mixed Acids

To dissolve the austenitic stainless steels, a mixed acid is usually considered. Mixtures of HNO_3 and H_2SO_4 increase the dissolution rate of the steels by about a factor of four over HNO_3 alone (7, p. 243); however, this combination is rarely used in pickling operations. The most commonly used solutions for pickling austenitic stainless steels contain HNO_3 and HF. The effect of this mixed

[4]"S" means lower carbon content to prevent carbide precipitation.

acid on various austenitic steels has been extensively studied and adequately reviewed (37). HF significantly increases the rate of dissolution of austenitic steels in HNO_3 solutions. For example, as little as 0.5 wt pct HF in 18 wt pct HNO_3 can increase the dissolution rate of 304 stainless steel by two orders of magnitude at 60° C and by almost three orders of magnitude at 80° C (37). This corrosion rate is approximately 15,000 μm/yr at 80° C.

Temperature

The above results suggest that temperature has a significant effect on the dissolution of austenitic stainless steels. A study (37) conducted on 309SCb[5] stainless steel indicated that a temperature change from 20° to 100° C increased the dissolution rate in HNO_3-HF solutions by over two orders of magnitude. This response to increasing temperature was shown to be true regardless of solution compositions from 4.5 wt pct HNO_3 + 0.2 wt pct HF to 27 wt pct HNO_3 + 2 wt pct HF. These results imply that the activation energy for dissolution is not affected by solution composition, although the absolute magnitude of that dissolution rate was found to be affected by solution composition.

CHROMIUM-DEPLETED ZONE DISSOLUTION

The dissolution behavior of the chromium-depleted zone should be affected by the same factors as those affecting the bulk steel: temperature, acid concentration, and agitation. Dissolution rates should be higher than those for the bulk steel because of the reduced chromium and nickel contents. Direct studies of the dissolution behavior of this depleted zone have not been conducted because of the extreme thinness of this zone. Indirect studies, however, have been done by fabricating alloys that simulate different regions of the depleted zone. A study (38) of a series of iron-chromium-nickel alloys (2 to 18 wt pct Cr) showed that the dissolution rate in sulfuric acid was high for very low concentrations of chromium. Surprisingly, however, the dissolution rate passed through a minimum at 12 wt pct Cr where the dissolution rate was only 40 pct of that for a 19 wt pct Cr alloy. Studies of similar alloys in HNO_3-HF would be very important for developing an understanding of the pickling of stainless steels. Equally important would be studies of the effect of acid concentration, temperature, and agitation on the dissolution behavior of these chromium-depleted alloys.

RESEARCH NEEDS

Based on this review of the literature on the pickling of stainless steels, the following areas have been identified as needing further study:

1. The effect of hot working on the grain size of metal and subsequent oxide scale composition.

2. The effect of annealing parameters such as furnace environment and time at temperature on the annealing scale and ultimately on the pickling rate.

3. The effect of the various conditioning techniques on the structure and composition of the scale related to its effect on pickling rate.

4. The dissolution behavior of bulk steels and the chromium-depleted zone of bulk steels, and the effects of the pickle bath variables, acid concentration, temperature, and agitation, on the dissolution rate.

In conclusion, additional studies in any one of the above four areas will contribute to the understanding of the pickling process. However, knowledge from all four areas is necessary to develop the relationships needed to quantify the

[5]"S" means lower carbon to prevent carbide precipitation, and "Cb" means niobium (columbium) added to prevent carbide precipitation.

pickling process. This quantification should lead to an improvement in the efficiency of pickling, a reduced cost to process stainless steels, and minimizing the loss of critical metals such as nickel and chromium. Laboratory studies are presently being done to understand the effect of acid concentration, temperature, and dissolved metal concentration on the pickling of 304 and 430 stainless steels.

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