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Surface Chemistry–Based Defects on Steel Sheet, Investigated by SEM/EDS

Throughout the steel manufacturing process, surface irregularities can occasionally occur. These are undesirable and may cause rejection or downgrading of the affected coil. Some of these irregularities, or defects, are purely topographical and are only due to (subtle) local differences in surface roughness or texture.[1] Such defects are sometimes caused by lubrication issues and, in that sense, can be indirectly linked to the chemical nature of the lubricant, but the defect itself is not characterized by local differences in chemistry. In contrast, other defects are clearly characterized by a deviating surface chemistry. This is the subject of the present paper.

Defects characterized by deviating surface chemistry can be subdivided according to: (1) where in the steelmaking process they occur, (2) how they appear to the naked eye, (3) the local environment in which they are formed, (4) the chemical compounds they consist of and (5) how they appear on a microscopic scale. To expand on these aspects:

1. Chemistry-related surface defects can occur in nearly all process steps in the steelmaking processes, from hot rolling and pickling (scale), cold rolling (staining), annealing (discoloration) to wet temper rolling (staining) and storage and transport (staining, corrosion, rust). Sometimes a (mild) defect may disappear during a downstream process, but others, such as scale, may irreversibly affect surface appearance. In this paper, a separate section is dedicated to an analysis of where these defects can occur in the steelmaking process. Note that the scope of this paper is restricted to defects encountered in and around the cold rolling, annealing and the wet temper process, and on coated steel (tinned/galvanized) as far as corrosion is concerned.

2. The manner in which these defects appear to the naked eye may also differ significantly. First, they can differ according to their color: mostly varying shades and intensities of brown/yellow are found, but also reddish, dark brown, gray or even black defects occur. Second, they can differ according to their shape and size: spots of varying size and shape can be observed, or patches that are irregularly shaped or with straight boundaries in the process direction; but there are also cases in which the entire surface is more or less homogeneously affected. Third, the defect boundary may be either sharply defined or be more diffuse in nature.

3. The local environment in which these defects are formed can be characterized by temperature, presence of moisture, atmospheric humidity, oxygen content, acidity, and the presence of other chemical compounds, either originating from the process fluid(s), or unintentionally, e.g., due to surface contaminations or contaminations in the process fluid. The local environment can also be characterized by the presence of crevices in which corrosion often occurs

Cold-rolled and wet-tempered steel sheet sometimes shows surface discoloration. This occurs in spots, patches or bands, and may have a range of possible causes. The discoloration may be caused by local differences in light refraction or light reflection off the surface. These differences may be caused by subtle oxidation processes, by corrosion resulting in the creation of etching holes or a thin oxide layer, by surface reactions, by deposition of compounds other than oxide or by a coating defect. Several field cases are discussed.

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preferentially,[2,3] or simply by the locations where, due to capillary forces, moisture may accumulate. During annealing, the environment may consist of pure hydrogen, or of HNX, a mixture of hydrogen and nitrogen.

4/5. Chemistry and microscopic morphology will be discussed in more detail in the next section.

It is often the combination of these five aspects that allows a full assessment of the cause of the defect and, through that, establish possible ways to address the issue.

The terminology used to identify (chemistry-related) surface defects is often highly subjective and has often developed specific to different steel manufacturers or even mill operators. Therefore, there is no clear and universally accepted system for identification (or nomenclature) of these defects. This should be kept in mind when the various defects are introduced in this paper.

Chemistry and Morphology

Chemistry-related defects can vary in composition, although they are mostly oxides. Nevertheless, other compounds can also be found, such as (polymerized) components of the process fluid, carbonaceous residues, or carbon, and sometimes components present in the makeup water, such as chlorides. Most often, chemistry-based defects consist of reaction products with the steel substrate, but occasionally they simply consist of deposited "alien" matter, i.e., contaminations like soaps, grease, particles of rubber or plastic, or accumulated iron fines.

Chemistry-related defects that can occur on steel sheet do not cover only a wide range of visual appearances; their microscopic appearance, as observed for instance with a scanning electron microscope (SEM), can also vary significantly. Particularly where corrosion products are involved, there are some frequently occurring features. Corrosion products quite often have the appearance as shown in Fig. 1a: smooth, globular structures that have a clear pattern that suggests a meandering growth over the surface, now and then interrupted by small holes and cracks (see inset). These structures consist of oxides. A possible explanation of the small holes is that under aqueous conditions, the oxides were deposited as a hydrated gel,[2] which was subsequently locally ruptured due to the evaporation of the water. These structures are often characteristic for atmospheric corrosion. It is also often found that the oxides have developed a cracked morphology, as shown in Fig. 1b, likely also formed during drying.

Locally, quite severe corrosive conditions can occur, which are often accompanied by widespread etching. These are tiny holes of submicron dimensions that usually start off individually, but can grow to larger sizes and join to create significant cavities in the surface (Figs. 1c and 1d). The pattern of the etching holes in Fig. 1d suggests that the etching holes have likely developed along grain boundaries. Etching holes are the result of a corrosion process in which the corrosion products were soluble, e.g., in a locally acidic environment. This leaves behind the etching holes where the metal has disappeared, while the corrosion products may have been deposited elsewhere. Local acidic conditions can occur in cases where anodic and cathodic regions are separated, e.g., in case of crevices.[3]

At high magnifications, sponge-like porous structures are sometimes seen, as shown in Fig. 1e. The exact nature and mechanism of formation of these structures is not known, but organic material is sometimes involved, as well as oxides. It is possible that some of these structures form in between windings in a coil, which are ruptured when opening the coil. The porous nature of the material that had grown between the windings is then revealed.

Oxides, when present on the surface, e.g., after cold rolling, or even due to rolled-in scale, may be chemically reduced by the environment present during annealing. This leads to the formation of metallic iron and the disappearance of bound oxygen but leaves the deviating morphology of the former oxides largely intact. This is illustrated in Fig. 1f. Some of this deviating morphology may survive the next processing step, e.g., wet temper rolling, leading to surface defects attributable to oxidation/corrosion/scale, but without the oxygen levels normally found in oxides.
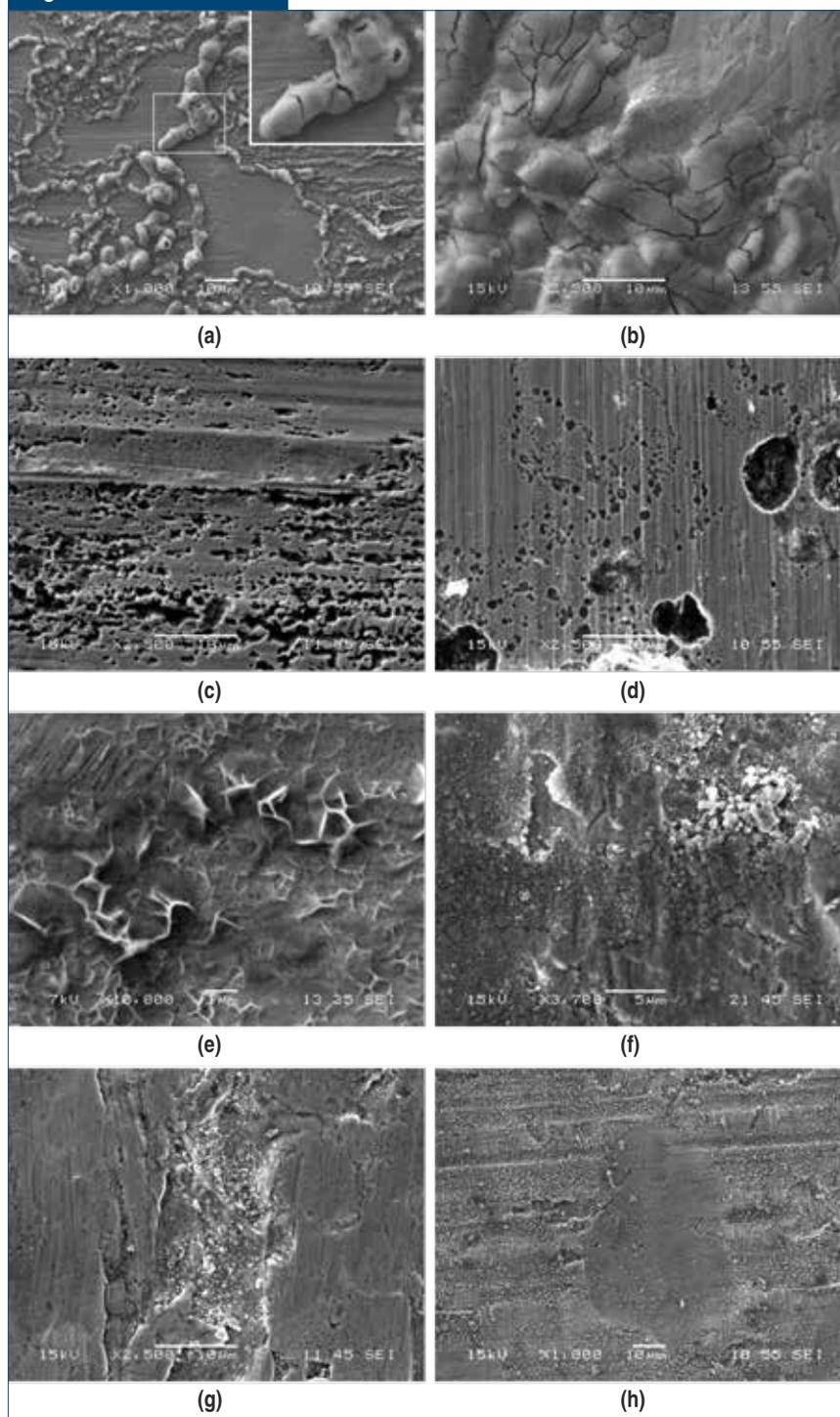
Sometimes, the oxides have a very irregular, broken-up appearance. This is illustrated in Fig. 1g. This appearance is mostly evidence of damage to the oxide structures due to a downstream process step.

Fig. 1h shows an example of submicron particles on a cold-rolled surface that were flattened into the general surface by the wet tempering process. This kind of evidence can be used to conclude that these features did not result from the wet temper process, but were created upstream.

Oxidation-induced staining is sometimes so subtle that oxides can hardly be detected at the surface, despite the discoloration being clearly visible. This can be due to very low oxygen levels in the environment, low reaction rates or only very short times available for this reaction.

There is often debate on whether a defect should be identified as "staining" or "corrosion." Both lead to defected surfaces (local variations in reflection and/or color). Staining can be defined as occurring

Figure 1

(a)   (b)

(c)   (d)

(e)   (f)

(g)   (h)

Examples of the morphology of some chemistry-related defects on steel.

when staining leaves the macroscopic surface morphology intact, but leads to submicron etching holes, and some settling of oxides. In such cases, staining can be considered as mild oxidation. A simple wiping test with dilute hydrochloric acid can sometimes be useful to distinguish oxidation-induced staining and reactions with other compounds (such as sulfur), the acid dissolving the oxides.

As mentioned earlier, in this paper defects on tinned/galvanized steel are limited to those involving corrosion. This means that coating defects themselves are not included. Pinholes within the coating and cavities on coated steel do sometimes expose the presence of alien matter, but it is often impossible to conclude whether these substances (i.e., oxides) are the cause or the result of the presence of the holes: oxides could interfere with the wetting of the molten tin or zinc, but oxides may also form if, due to a coating defect, the steel surface is locally exposed to air.

The Interaction of Light With Surfaces

When surfaces contain defects (spots, lines, stains, etc.), it means that there are spatial differences in the manner in which incoming light reflects off the surface and/or the color of this light. These differences are perceived by the observer as an undesirable surface deviation. In order to fully understand such surface defects, it is helpful to consider the physical background behind the interaction between incoming light and a surface, and how the nature of the surface influences the nature of the reflected light. With regard to the surface defects discussed in this paper, four aspects should be distinguished: (1) reflection off (metallic) surfaces, (2) refraction in (semi-) transparent media, (3) absorption of certain

through reactions of the steel surface with any reactant (oxygen, water, sulfur, phosphorus, etc.), but — crucially — leaving the substrate morphology intact. Corrosion can be defined as occurring through oxidative reactions (oxygen or water), leading to significant deposition of oxides and/or strong substrate damage. As usual, gray areas exist, e.g.,
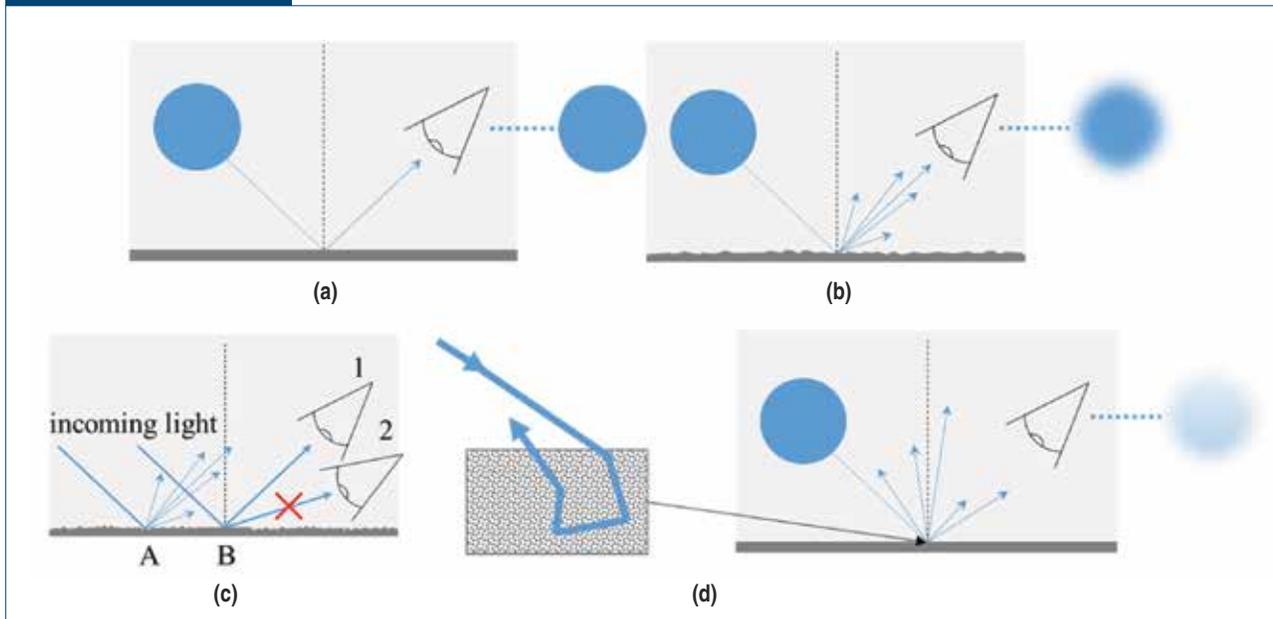
Figure 2

Illustration of specular and diffuse reflection, depending on the surface roughness (a,b), illustration of the brightness with which a smooth spot B (at the center) on an otherwise rough surface A is perceived (c), and illustration of severe light scattering occurring within some materials, which can be conceived as an extreme form of diffuse reflection (d). This is sometimes the reason for the white appearance of some materials, i.e., having the color of the scattered (white) light.

wavelengths in (semi-) transparent media and (4) interference (leading to disappearance of certain wavelengths). These aspects are discussed briefly below and also in Reference 4.

1. Completely flat, polished surfaces reflect light according to Snell's law, which states that the angle of reflection equals the angle of incidence. This is sometimes referred to as specular reflection. This is illustrated in Fig. 2a. Objects reflected off such surfaces appear as perfect mirror images. In case the surface is not completely smooth (i.e., it has a certain roughness), incoming light is reflected in many directions. This is called diffuse reflection. Objects reflected off this kind of surface appear (slightly) more blurred, with indistinct boundaries. This is illustrated in Fig. 2b. With regard to surface defects, the appearance of the surface itself is actually the most important: the surface in Fig. 2a having a brighter appearance, and the surface in Fig. 2b a (slightly) more matte, or dull, appearance.

    On surfaces with local variations of light reflection, e.g., due to the presence of areas of lower roughness, it is sometimes difficult to qualify these smoother areas. They usually appear darker than the general surface, but when viewed at another angle with respect to the incident light, may seem lighter. This is due to the fact that, at most angles of incident light, the light reflected off the spot misses the eye and the spot will appear darker (less light reaches the eye). When observing the spot area roughly at the angle of reflection, the spot will seem lighter. This is schematically illustrated in Fig. 2c: smooth spot B is perceived lighter for observer 1 than the surrounding, rougher area A, as light is reflected more specularly at B for this observer. For observer 2, area B appears darker as little light is reflected toward his position, and more light is actually received from area A.

2. The manner in which light reflects off the surface depends on not only the surface roughness but also on the nature of the material. For instance, a piece of chalk may be completely smooth, yet it is still unable to display specular reflection. This is due to interaction of the light with internal microstructures (grains, air bubbles, etc.), resulting in severe light scattering. This is illustrated in Fig. 2d. This mechanism is also often the reason that oxides (rust) can appear white whereas others appear dark, even though they are composed of similar chemistry. In case oxides have a porous structure, they often strongly scatter light (similar to Fig. 2d) and appear white. In contrast, when oxides have a dense structure, they may reflect light more specularly and thus appear darker.

This is often the reason for the appearance of rust on zinc, which may be gray or white.

3. A further aspect that needs to be considered is the surface color. Colored surfaces normally appear colored due to the absorption of certain wavelengths of the incident light by the material the surface consists of. This is due to the molecular composition of the surface material. For instance, the red pigments in a red paint absorb all wavelengths except red, so that the reflected light contains only the red light wavelengths.

4. A surface may also appear colored due to an interference phenomenon that cancels out certain wavelengths of the incident light. This interference phenomenon is found when a thin (semi-) transparent layer is present on top of a reflective surface, such as a thin oxide layer on the metal. The incoming light will reflect off the oxide surface, as well as off the underlying surface. When the waves recombine at the surface they may cancel out or reinforce one another. Depending on the oxide thickness and the wavelength of any one of the light waves that constitute the incoming light, certain specific frequencies will be cancelled out, leading to the loss of certain wavelengths in the reflected light. Mostly incoming light is white, so this loss of certain wavelengths means that the light reflected off the surface will have a color, i.e., the surface is perceived as colored. This is often the explanation for the color of (mild) oxidative staining on steel surfaces.

Methods for Identification of Surface Chemistry–Based Defects

Surface defects can be assessed with several techniques, from the simple to the very advanced. Some can be used to visualize the defect and some to obtain information on the chemical composition. The most powerful techniques combine the two. Many surface defects have their origin in local variations of light reflection off surfaces, as seen above. Due to the fact that the surface features that give rise to these local variations are often very small, scanning electron microscopy, with its high spatial resolution, is mostly the preferred technique, especially when combined with energy-dispersive x-ray spectroscopy (EDS).

In the SEM, a beam of electrons is focused on a sample in a high-vacuum chamber. The beam releases electrons from the atoms in the sample (secondary electrons), which are detected by the secondary electron detector. The amount of electrons thus detected as the electron beam scans the surface gives an image of topography, including, e.g., shadow effects, and a photorealistic image of the surface morphology is created. Electrons from the electron beam that are scattered elastically from the sample are detected by a backscatter detector. The amount of electrons thus scattered depends on the material density (atom number) and thus, with this detector, some qualitative elemental information can be obtained.

EDS gives the chemical composition on the element level. An EDS signal arises when the positions in the atom shell of the secondary electrons released by the primary electron beam are reoccupied by higher-lying electrons in the atom. This process is accompanied by emission of x-rays. The energies of these x-rays are characteristic for every element. The resulting EDS spectrum can also be analyzed quantitatively.

It is the authors' experience that SEM/EDS is suitable for analyzing most surface defects encountered in the steelmaking industry. In rare cases, other techniques such as x-ray photoelectron spectroscopy (XPS) are required to elucidate surface chemistry to even higher detail. Occasionally, Fourier transform infrared spectroscopy (FTIR) is required to analyze surfaces contaminated with organic matter. FTIR is a well-established technique in analytical chemistry to obtain the chemical nature of (unknown) compounds. The technique is based on excitation of stretching and bending resonances of chemical bonds by wavelengths in the infrared region of the electromagnetic spectrum. An attenuated total reflection (ATR) cell allows for easy FTIR analysis of surface chemistry as measurements are directly done on the contaminated sample.

In this report, surface analyses were carried out with an SEM (Jeol 6480) equipped with an EDS system for surface elemental analysis (Genesis Si(Li) and in later studies Apollo SDD system by EDAX), and an FTIR spectrometer (Bruker Tensor 27) fitted with an ATR cell or a variable angle specular reflectance cell (VeeMax II from Pike).

Types and Occurrence of Surface Chemistry–Based Defects

During the production of flat steel products, the steel undergoes a series of processes to achieve the required metallurgy, thickness, surface roughness and texture. Following hot rolling of steel slabs or continuously cast steel, and a pickling process to remove the surface oxides, the steel is cold rolled in a series of consecutive reduction steps. Thereafter, the steel is annealed, after which a series of final production steps follow to provide the product with the right surface roughness, texture and, if needed,

a protective coating (e.g., zinc, tin, zinc/nickel, zinc/aluminum).

Surface defects can occasionally occur in flat steel production due to the large number of production steps, the critical conditions that need to be maintained in each of these steps, the numerous steel alloys being produced and the fact that the steel surface is exposed to different process fluids. Many of these defects are purely topographical, as discussed in an earlier paper on steel surface defects.[1] On the other hand, of nearly 500 examined defect cases, two-thirds (330 cases in total) appeared to be chemical in nature. These can be subdivided in surface oxidation, process fluid reactions (polymerization, carbonization), contamination and element migration. In the field, surface defects are mostly noticed by automated in-line camera equipment with fast image processing software involving bright- and/or dark-field illumination, or a combination of both, to detect defects most effectively.[5]

In bright-field illumination, the charge coupled device (CCD) camera captures most of the directly reflected light, resulting in a bright surface with defects appearing darker in the image. In dark-field illumination, the angle of the incident light with the surface is very small, yielding a dark appearance of the surface, with certain defects appearing brighter. As image-processing software is generally not suitable to classify defects properly, additional visual inspection is often necessary. In some cases, however, this may lead to misidentification of the defect because visual appearance is not always indicative of the chemical nature of the defect. Therefore, as discussed earlier, surface chemistry analysis is often required to provide conclusive data about the chemical nature of the defect. It appears that the number of surface chemistry–based defects belonging to the scope of this report is basically limited to surface oxidation, reactions of the surface with the process fluid, surface contamination with alien matter and element migration. In the field, identical defects are often indicated by different, rather descriptive names (e.g., mold streaks, streak black lines and aluminum streaks, all three indicating the same defect). On the other hand, identical names are sometimes given for different defects (e.g., a black streak defect may represent rolled-in scale or a steel alloy inclusion defect). In Table 1, an overview of types of surface chemistry defects, including possible causes, is presented. Note that hot rolling and pickling defects, as well as defects caused by the passivation process, are not the scope of this paper. This overview, while based on 330 SEM/EDS analyses carried out over a 10-year period, does not pretend to be complete nor fully representative of all defects that occur in steel cold rolling. It should also be emphasized that SEM/EDS analyses do not always reveal the root cause of surface defects, but on the other hand, most analyses were very helpful in finding the possible cause of the defect and in advising the customer on how to solve the problem.

As shown in the table, all process steps occasionally suffer from the occurrence of surface chemistry–based defects. Corrosion/oxidation is, not unexpectedly, the most widely occurring defect. Second in occurrence are defects caused by contamination of the steel surface with alien matter such as calcium soaps, iron fines, dirt and scale. Note that in many cases where alien matter was rolled in, the deviating surface chemistry of the defect is accompanied by morphology changes of the underlying steel surface as well. This means that after cleaning defect spots with a solvent, a roughened surface often emerges, which may be due to the presence of so-called transverse fissures[1] or due to the presence of etching holes ("pinholes"), formed by a mild, local corrosion process. As a third defect category, residues should be mentioned, originating from carbon sediments (snaky edge), incomplete evaporation and degradation of the rolling oil (carbonaceous residues) or by other reactions in the process fluid(s). Finally, migration of carbon or other alloy elements from bulk to steel surface is occasionally found after annealing.

In Fig. 3, the relative contribution of the different process steps to the occurrence of chemistry-based surface defects during/after steel cold rolling is presented, based on the same 330 SEM/EDS analyses. Most often, with nearly 45% of all cases, defects of the cold-rolled strip surface are reported. Second in frequency, with almost 20% of all defects, are those observed after annealing. Wet temper defects and defects after oiling both contribute to approximately 15% of all surface defects, and defects on tinned/galvanized sheet occur in slightly more than 5% of all defect cases. In the next section, a few examples of surface chemistry based defects will be discussed.

Examples of Defects

Cold Rolling — Corrosion — Most surface chemistry defects that occur on full hard steel concern corrosion caused by coiled-in rolling emulsion left behind on the surface due to an insufficient blowoff or suboptimally functioning wipers. Subsequent storage of the coils may then result in corrosion in the shape of oxide spots or bands of more or less severe staining. In some cases, the corrosion process was triggered by traces of chlorine originating from the pickling process (acid carryover) or by salts originating from the water used to prepare the rolling emulsion. An example of full hard strip corrosion due to acid carryover is presented in Fig. 4. Here, a 6- to 7-cm-wide

Table 1

Overview of Different Types of Surface Chemistry Defects for Each of the Cold Rolling Process Steps, for a Series of ~330 SEM/EDS Analyses Performed Over the Last Decade

Process	Defect (visual appearance)	Chemistry	Cause
Cold rolling (44%)	Gray to brown spots, bands or patches, irregular cauliflower-like spots, faint light gray shades or bands	Surface oxidation	Coiled-in emulsion due to insufficient blowoff, poorly functioning wipers or emulsion carryover
	Brown spots	Surface oxidation	Atmospheric corrosion/too long coil storage
	Large, smooth, brown spots and areas, spots with cauliflower-like boundaries, brown band along edges	Surface oxidation	Presence of chloride/salts in the rolling emulsion due to makeup water quality problems or pickling bath acid carryover (sometimes combined with emulsion carryover)
	Homogeneous brown staining	Surface oxidation	Too-high strip temperature (sometimes also resulting in oil polymerization)
	Small, dark gray spots, irregularly distributed	Contamination with alien matter	Calcium soaps, formed as a result of poor makeup water quality or emulsion contamination with Ca-based grease
	Dark gray-black spots	Contamination with alien matter	Rolled-in scale due to incomplete scale removal during pickling or scale residues due to damaged hot mill work rolls
	Whitish, gray, black spots, irregularly distributed	Contamination with alien matter	Rolled-in oily dirt, iron fines, paint particles, grease, other alien matter
Annealing (33%)	Snaky edges/carbon edges	Process fluid reactions	Deposition of elementary carbon due to decomposition of methane close to the strip edges (insufficient sulfur in the rolling oil, type of annealing gas mixture)
	Black spots, streaks	Process fluid reactions	Carbonaceous residues due to incomplete annealing (too thick rolling oil layer, unsuitable rolling oil chemistry, too short annealing cycle, type of annealing gas mixture)
	Straw yellow to bluish surface	Surface oxidation	Strip surface exposed to air while still too hot
	Small brown spots	Surface oxidation	Traces of chloride, sulfate or salts in the rolling emulsion due to poor makeup water quality or pickling bath acid carryover
	Grayish spots and patches	Contamination with alien matter	Rolling debris or dirt entrained in the roll bite and annealed
	Small black spots	Migration of alloy elements	Carbon migration to the surface in case of steel alloys with low sulfur content, no sulfur in cleaning bath
	Bluish discoloration of the surface	Migration of alloy elements	Migration of alloy elements to the surface, such as manganese
	Small, freckle-like spots	Migration of alloy elements	Iron carbide precipitation due to a too-high annealing temperature (1,330°F, 720°C)
Tinning/galvanizing (15%)	Whitish spots	Surface oxidation	Corrosion of zinc coating due to coiled-in moist (temper fluid)
	Brown spots	Surface oxidation	Corrosion of the underlying steel due to insufficient coverage by the tin layer or due to pinhole defects
	Whitish streaks	Contamination with alien matter	Dirt from guide rolls
Tempering (15%)	Large brown patches, bands	Surface oxidation	Coiled-in temper fluid (insufficient blowoff)
	Brown specks/spots	Surface oxidation	Insufficient time between annealing and tempering (not enough time to passivate the steel surface)
	Brown specks/spots	Surface oxidation	Too long time between tempering and oiling
	Brown specks/spots	Surface oxidation	Airborne salt particles (coastal areas)
	Grayish spots and patches	Contamination with alien matter	Guide rolls before temper fluid application contaminated with iron fines/oxide dust
Oiling (16%)	Large yellow or brownish spots	Surface oxidation	Insufficient protective oil, inhomogenous coverage by the protective oil
	Brown, yellow, grayish specks, larger spots	Surface oxidation	Moist surface covered with protective oil due to insufficient blowoff of (salts-containing) temper fluid
	Irregular brown spots, bands	Surface oxidation	Airborne salt particles (coastal areas)
	Yellowish/brown spots and patches	Process fluid reactions	Reaction of temper fluid remains with the rust-protective oil

Figure 3
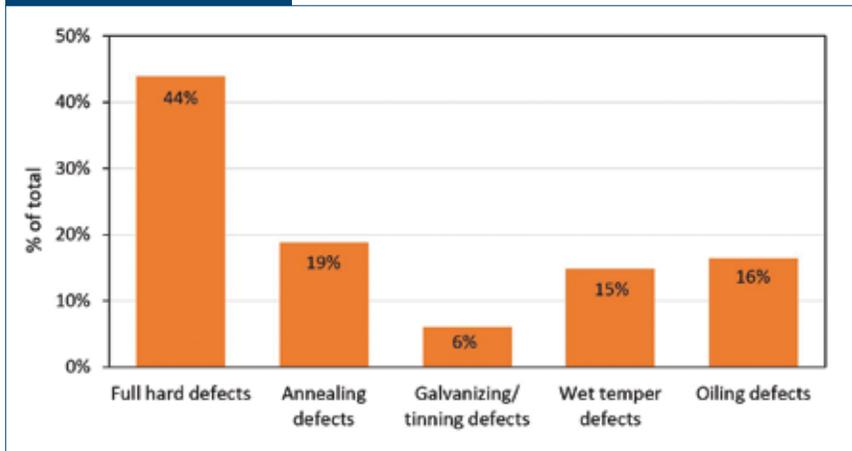
Relative contribution of the different process steps to the occurrence of chemistry-based surface defects during and after steel cold rolling.

Figure 4
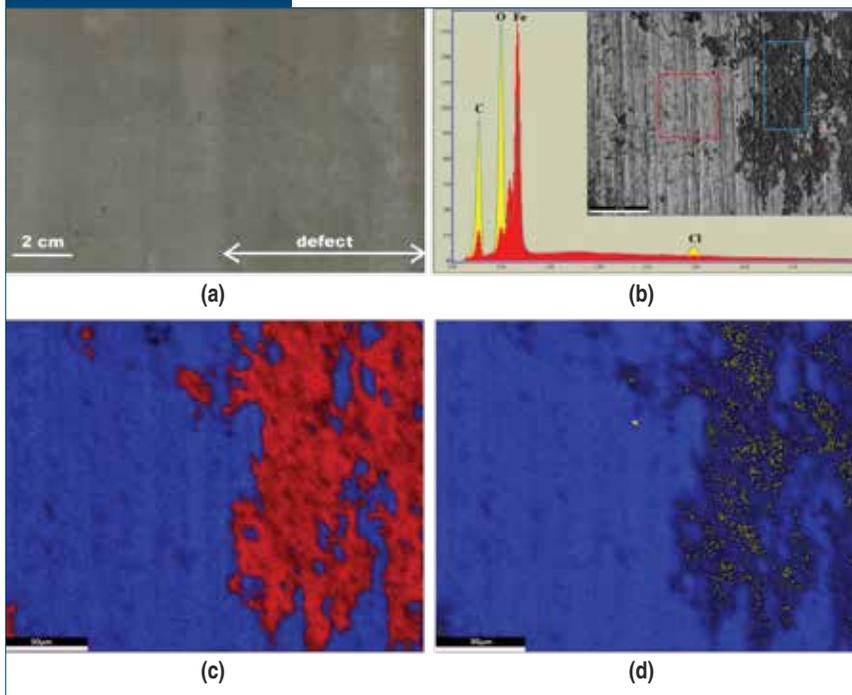
Visual appearance of a grayish-brown band of staining on full-hard steel (a), energy-dispersive x-ray spectroscopy (EDS) spectra of a staining spot (blue outline) and of adjacent non-stained surface (in red) (b). The inserted image shows a backscatter image comprising both surfaces. The stain contains more oxygen, carbon and a significant amount of chlorine. Element map for iron (in blue) and oxygen (in red) (c) and element map for iron and chlorine (in yellow), of the same surface area (d). The area comprising chlorine closely matches the area with elevated oxygen levels.

band of grayish-brown staining was observed close to the strip edge. An EDS spectrum of a small oxide spot, observed under high magnification, reveals the presence of a high amount of oxygen and, due to the porous nature of the oxide, a high amount of carbon (representing rolling oil remains). Closely associated with the corrosion spot is the presence of a relatively high amount of chlorine, which may have accelerated the corrosion process.
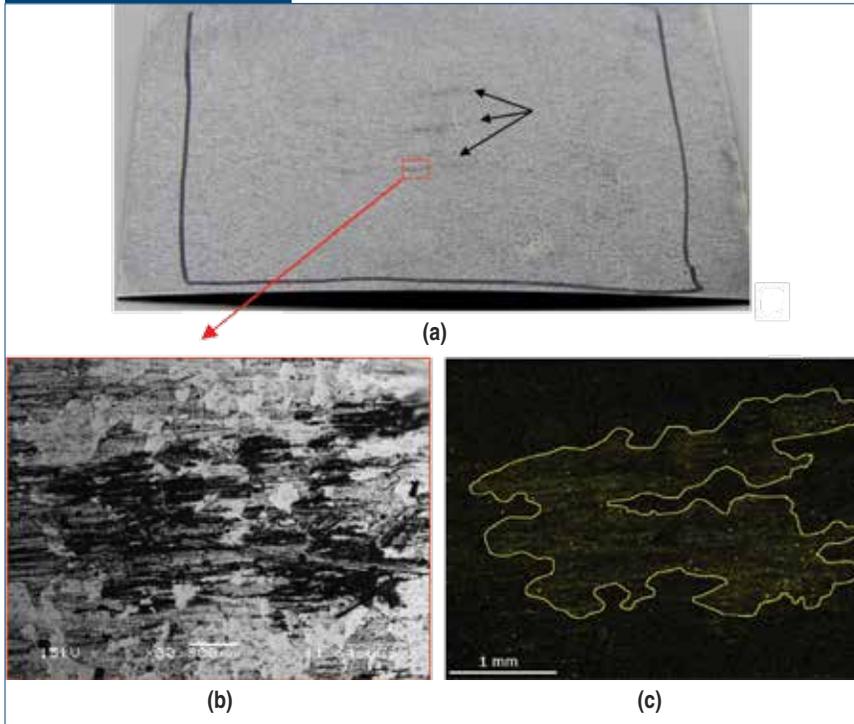
Cold Rolling — Rolled-In Calcium Soaps — Less frequent than corrosion defects, but not uncommon, are surface chemistry defects caused by rolled-in alien matter, such as iron soaps, calcium soaps or oily dirt comprising metal fines, oxide matter, or other contaminants (e.g., paint particles, filter material, sand, etc.). An example of a surface chemistry defect associated with calcium soaps is depicted in Fig. 5.

In this case, a Ca-containing bearing grease had contaminated the rolling emulsion, leading to the formation of small, sticky lumps of calcium soap. These were trapped in the roll bite, resulting in small, black, elongated spots on the full hard strip surface. By means of EDS element mapping, these kinds of defects can be easily identified. As shown in Fig. 5c, an element map clearly demonstrates that the alien matter comprises a significant amount of calcium. This could point to either calcium present in the water used to make up the rolling emulsion or to contamination of the rolling emulsion with a calcium-based grease. Analysis of the makeup water and of the bearing grease indicated that the bearing grease was the root cause of the defect.

Cold Rolling — Temperature-Induced Surface Oxidation — After the cold rolling process, the strip surface may show a (slight) discoloration over the entire surface, which is often due to (slight) surface oxidation. Not only is this undesirable and may lead to downgrading, it can also lead to quality issues downstream. In some cases, surface oxidation of the incoming steel has been

Figure 5

Visual appearance of black stains caused by rolled-in calcium soap (black arrows) (a), backscatter image of one of the stains, revealing the lower density of the stain matter (in black) (b), EDS map for calcium (in yellow) of the same surface area (c). The outline of the area comprising calcium closely matches that of the stain.
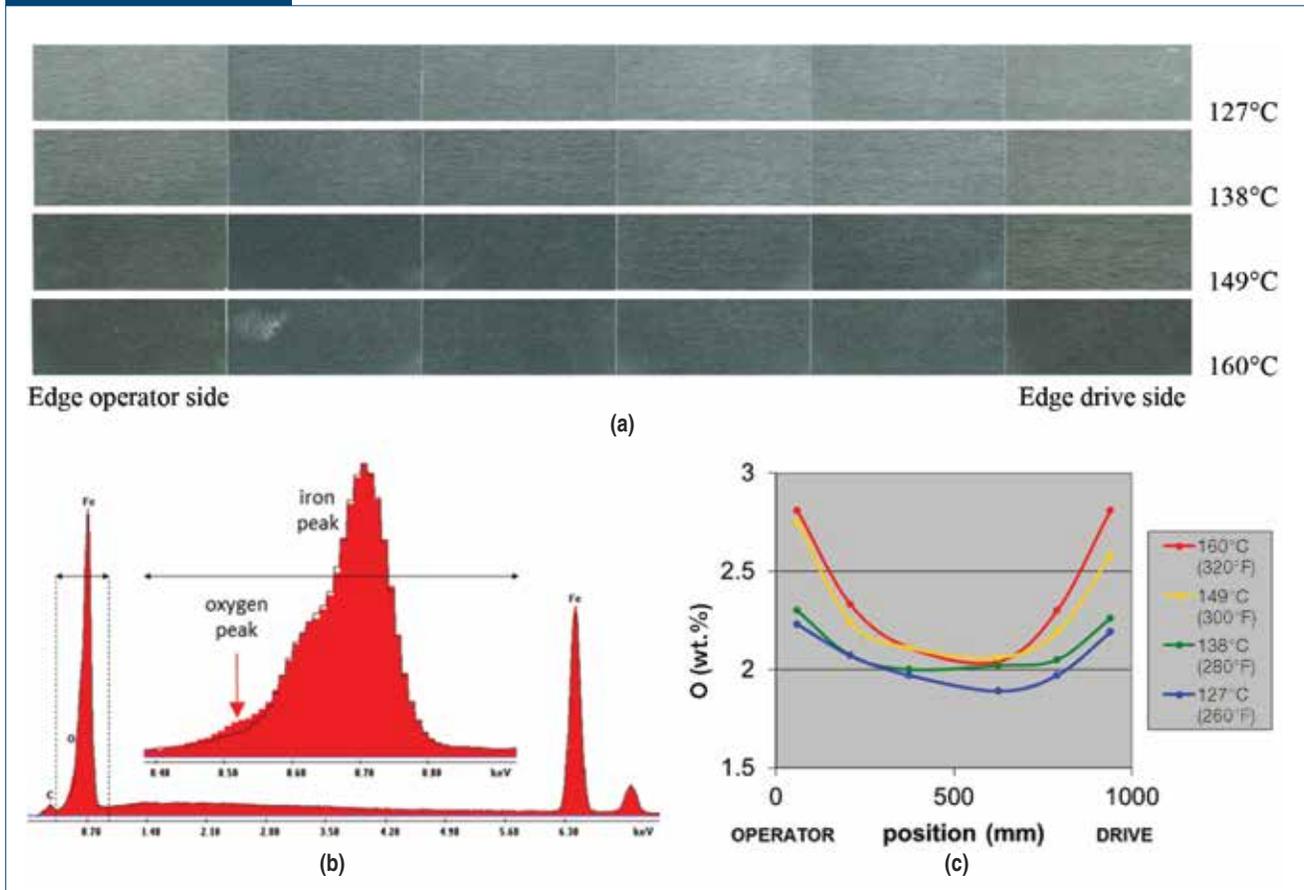
the organic components in the remaining rolling oil decompose into short-length alkanes, mainly methane. Under some conditions, and catalyzed by iron, the methane decomposes into carbon, which settles on the surface, and hydrogen gas. In case of high hydrogen levels in the annealing gas, this reaction is slowed down, which explains the usual preference for pure H_2 gas in annealing rather than HNX. The aforementioned catalytic action of iron is "poisoned" by the presence of sulfur, which is why sulfur compounds are usually included in the rolling oil. This defect can also be counteracted by introducing a constant temperature step in the annealing cycle (at lower than the maximal annealing temperature), which gives the organic molecules time to escape the coil without depositing as carbon.

In Fig. 7a, a typical example of a carbon edge can be seen (the edge of the strip is visible on the left). With the SEM, it can be seen that the carbon (i.e., the dark patches) is deposited irregularly on the surface (Fig. 7b). Figs. 7b and 7c show the flaky nature of the carbon, which may be due to a rupture process during opening of the coil.

Wet Temper Rolling — Staining — After the wet temper process, a particular type of staining sometimes develops, frequently called "brown staining." This staining occurs as long, straight, or slightly meandering bands of brown or yellowish discoloration, 10–30 cm wide, at the center of the strip. Sometimes a lighter band is found at the center of the staining. A typical example can be seen in Fig. 8a. The shape of the band is usually mirrored on the surface of the adjacent lap. The discolored areas are generally distinguished from the reference surface by a small but clearly increased oxygen peak in the EDS spectrum (Fig. 8e). On the microscopic scale, sponge-like structures can often be found, which are also mirrored on the surface of the adjacent lap. This corroborates the scenario discussed earlier in this paper ("Chemistry and Morphology"): the oxides form locally and fill the space between touching asperities, and are ruptured upon opening the coil.

The staining is the result of a mild corrosion process occurring in the coil, where it develops mainly in

suspected to be the cause of coating defects (of galvanized steel, Galvalume®, etc.). Surface oxidation may occur due to excessive exit strip temperatures after the cold rolling process. This has been studied systematically at a steel manufacturer by varying the strip exit temperature between 127°C and 160°C (260°F and 320°F). In Fig. 6a, it can be seen that the surface becomes darker/browner as the coiling temperatures increase. This effect is greatest at the strip edges, presumably due to the fact that these zones can be reached better by the atmospheric oxygen. Strip samples for every coiling temperature were obtained along the strip width and analyzed with EDS (at 15 keV). See Fig. 6b for a representative spectrum. The amount of surface oxygen was determined quantitatively and the result can be seen in Fig. 6c. It is confirmed that the oxygen levels (oxides) increase with coiling temperature and position closer to the edge. It also correlates with the surface discoloration. Please note that the oxygen levels should be interpreted in a qualitative sense only.

Annealing — Carbon Edge — After the annealing process, a carbon edge is sometimes found at the edge of the strip, also called snaky edge. This defect is the result of the deposition of carbon. At the high temperatures occurring during annealing,

Figure 6

Surface appearance of 30 x 10 mm steel samples taken at various locations between operator and drive side and rolled at different temperatures (a), EDS spectra of surfaces with the lowest oxygen level (black outline) and the highest oxygen level (in red) (b) and plot of the amount of oxygen along the strip width, for the various coiling temperatures (c). Oxygen data refer to the uppermost ~1 μm surface layer.

Figure 7
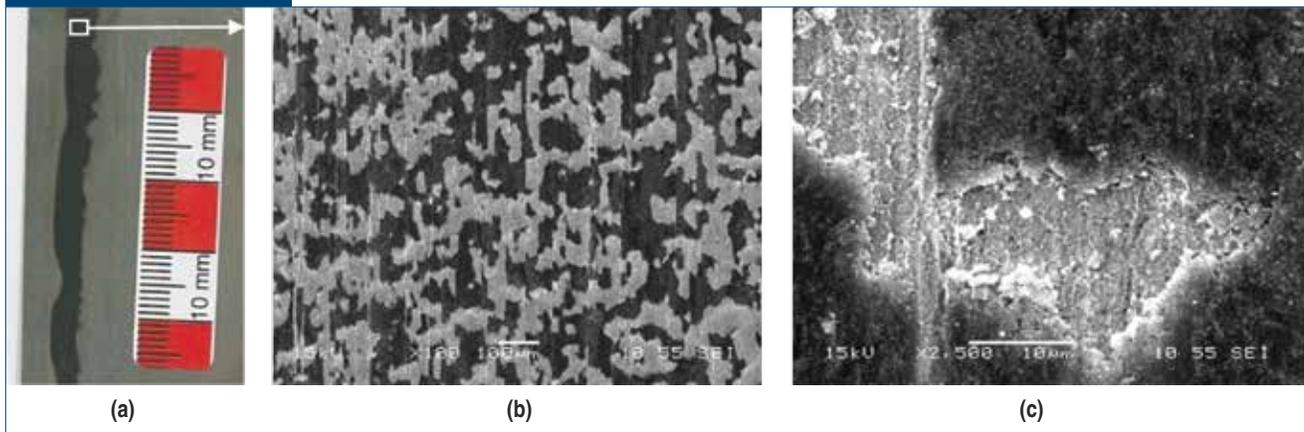
Example of a carbon edge (a), secondary electron images at 100x (b) and 2,500x magnification (c).

Figure 8
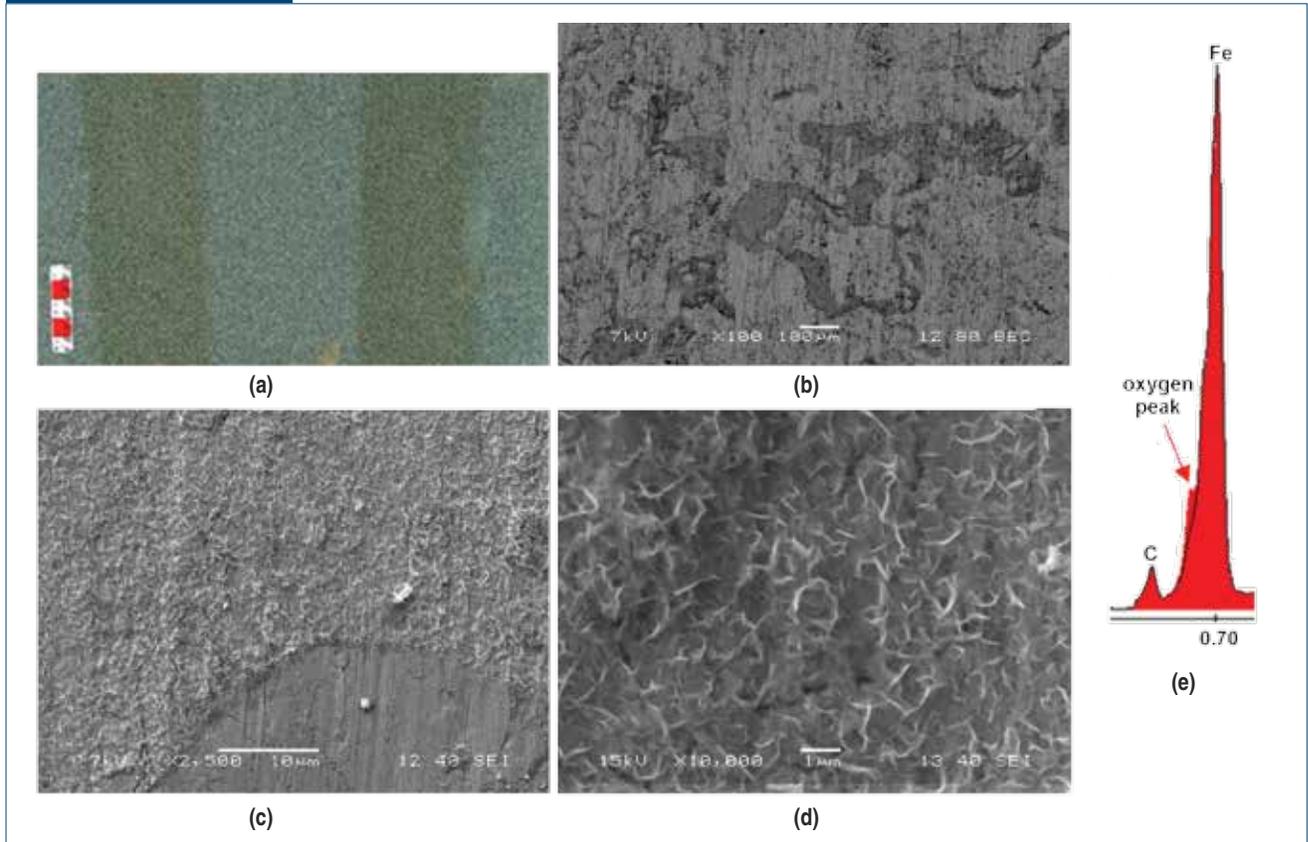
Typical example of wet temper staining (a) and its features discussed in the text. In (e), the EDS spectra of staining (red) and reference (black outline) are shown.

moist areas. Moist areas can be created by the migration of temper fluid to the narrowest spaces between the windings under the influence of capillary forces. The staining pattern, therefore, can be influenced by strip shape (crown). Moist areas may also be created by locally high fluid film thickness during the temper rolling process, for instance in the middle of the strip. This could be due to strip shape and work roll crown, which could, in turn, be affected by roll force.

In Fig. 8b, the areas of oxide appear slightly darker than the general surface (image obtained by a back-scatter detector, which shows less dense compounds as darker). The areas of oxide are also sharply delineated, which suggests that the oxides preferably form in the areas of close contact between the touching surfaces/asperities in the coil. This sharp boundary of the oxide areas is also shown in Fig. 8c. Finally, Figs. 8c and 8d show that the oxides occur in the form of sponge-like structures, for which the mechanism of formation remains unclear.

One contributing factor that can be hypothesized for this defect is the state of the surface as it is presented to the wet temper mill. If the storage time between annealing and wet tempering was too short, the passivation (reoxidation) of the annealed steel surface would have progressed insufficiently, and the surface would be very sensitive to oxidation/mild corrosion. The center of the strip is hardest to reach for reoxidation, which may contribute to the apparent higher sensitivity there. This also explains the higher sensitivity for staining when the coil is wound very tightly, i.e., with high coiling tensions. The passivation process may also depend on the humidity (fluctuations) in the atmosphere, which could explain the strong influence of certain climatic conditions on this defect.

Staining after the wet temper process may also occur as spots, blotches or irregularly shaped large patches. This staining may occur in the absence or presence of rust-protective oil, which is often applied after wet temper rolling. In some cases it was observed that remains of wet temper fluid that were insufficiently blown off had interfered with the rust-protective oil, either by displacement of rust-protective oil by the excess water, or by chemical reactions leading to the formation of, e.g., calcium compounds. In some cases, components from the

wet temper fluid could be identified on the oiled surface, by FTIR, measured directly on the strip surface with an ATR cell.

Conclusions

Surface chemistry–based defects are found occasionally after steel cold rolling and the processes further downstream. Despite the wide range of sizes, shapes, colors and reflectivity of these defects, the actual chemistry underlying these defects is quite limited. Most defects involve oxidation of the steel surface, chemical reactions within the process fluid, deposition of alien matter or element migration. Given the relatively simple chemistry of most defects, they can often be easily identified by means of SEM/EDS analysis. Combining the information on where in the process the defect occurred, the conditions under which these were formed, and the microscopic morphology and chemical composition of the defect, the root cause of the defect can often be deduced, and remedies suggested to the customer.

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