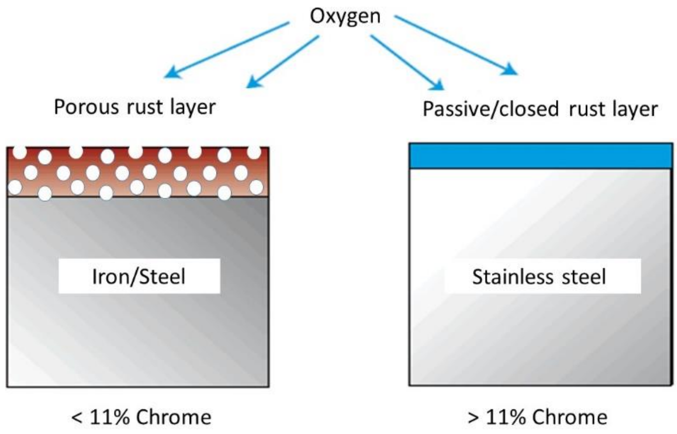
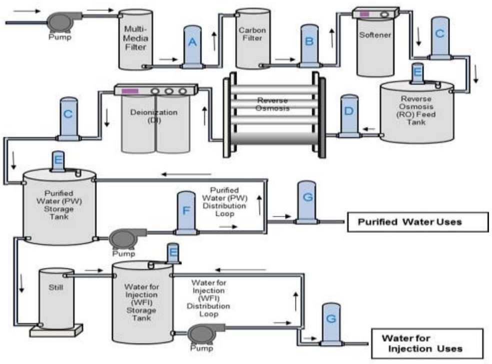
What is it about δ -Ferrite and *Rouging?*

By Cor Tiele – www.bpe-technology.com

In the Biotech and pharmaceutical industry stainless steel tube fittings and valves are widely used for transport. They are welded together by orbital (circular) TIG (Tungsten Inert Gas) equipment with closed welding heads. Like Carbon steel, Stainless steel does "rust" into the surrounding air. In contrast to the rust layer formed on iron, the layer at Stainless steel is not porous and it protects the underlying material against corrosive attacks. This is called the "passive" layer.



In the 90s investigations started into the discoloration in WFI (Water For Injection) and CS (Clean Steam) systems. Such discoloration depends on temperature and surface quality of the Stainless steel – with a range from golden to purple. This is called Rouging and it can only be removed mechanically.
Rouging has no negative effects on the quality of the water.

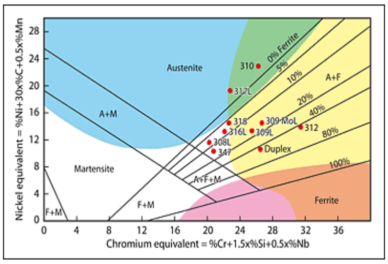


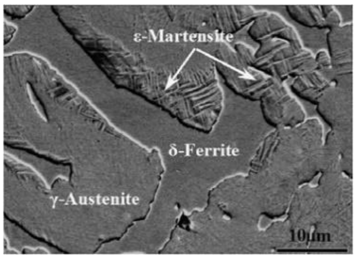
Left discoloration of the material surface and at the right after electro-polishing

In these industries, anything that can have an impact on the product purity/quality is defined in "procedures". In the event that Rouging occurs, there must be a procedure that describes the actions that take place in order to bring the system back to its original (and validated) state.

A difficult problem, because when you know that the discoloration does not adversely affect the quality of your water or steam, but removing the Rouge will shut-down a part of your process, when will you take action? This lead to creative solutions, like a Rouge-meter. A piece of pipe that could be inserted into an existing system which could measure the colour and thickness of the Rouge. So in the end there was, in any case, a "measured" value, for which procedures could be written.

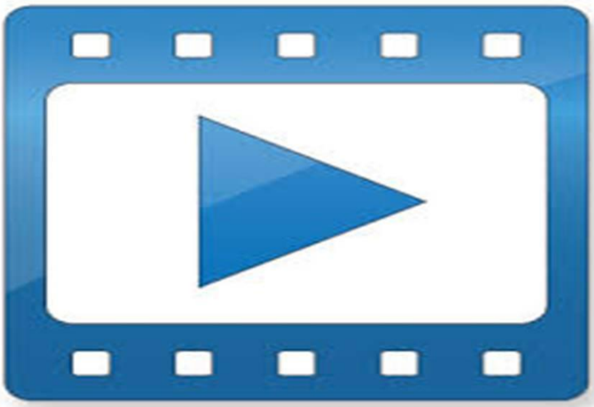
Until now there have been many studies and it is still unclear which mechanism causes Rouging. Although no concrete solutions are available, this article discusses the background, standards, recommendations, stories and tips ....





δ-Ferrite

δ-Ferrite is no ordinary Ferrite / Iron. It is formed during the cooling of the weld between 1492 ºC and 1400ºC and the quantity δ-Ferrite can be predicted in the Fe-C / Fe-FE_3C diagram. The formation and quantity after welding, can be reduced by the use of weld filler metal (in the form of weldrings of for example 904L), the material composition (indicated in a weight percentage of the alloying elements), and the shielding gas (addition of 2-4% Nitrogen).



Source YouTube: by Salar Niknafs - University of Wollongong. Delta -ferrite phase transformation observed with a High-Temperature Laser-Scanning Confocal Microscopy

The first time I heard of δ-Ferrite was during an IWT training. More clarity came in the late 90s when the Basler Norm 2 was published. A recommendation based on studies for the cause of Rouging between 1993 and 1998. The study focused primarily on the welds and HAZ (Heat Affected Zone) which was in those areas the largest amount and most discoloration was found. As they measured a higher ferrite content under the discoloration, the relationship Ferrite -> Iron -> Rust -> was easily made. The results of these studies were poured into a "Basler Norm II" and BN2 gave a recommendation to move from traditional AISI 316 with material number 1.4404 to 1.4435. This Stainless steel is compared to 1.4404 higher alloyed with Chrome (+ 0.5%), Molybdenum (+ 0.5%) and Nickel (+ 2.5%). Apart from the advantages with respect to corrosion resistance and mechanical properties, it was also easy to realize a low δ-ferrite content after welding with this material. Also we should not underestimate in this era that there was a believe that it was some kind of "insurance" against Rouging.

Late 20th and early 21st century the engineering firms and consulting organizations are flocking to adjust the material and welding specifications. Pharmaceutical companies demanded their new WFI and CS systems delivered with a low δ-ferrite content. In the beginning, the requirement was in accordance with the BN2 <0.5% and today is demanded even <5%. One difference with an unclear origin and therefore I suspect someone placed the dots wrong, and this specification is simply copied by others.

Additional studies

The results and recommendations of the BN2 lead to a number of scientific studies. At the Force (Technology) Institute in Denmark it turned out after several months of testing to be a lot simpler to investigate Rouge, as in order to make it.

For what conditions should they look at before the discoloration actual starts? They used plates with an MB/Metal Blank and EP/electro-polished surface, were for 6 weeks for 80% immersed in boiling WFI and then 3 days purged with air (with and without CO_2) or nitrogen.

This study was stopped after a few months because it was only possible to produce a small line of Rouge at the water line in the carefully prepared test. It was decided to publish the results (!) There was a significant difference found between the degree of discoloration at the MB and EP plates.

In the first 10 years of this century the Biotech and Pharmaceutical industry changed. From a closed market where problems/challenges were processed internal – to an industry that was looking with others to solutions. They searched together for knowledge and experience since many had Rouging in their buffer tanks, stills and steam generators. A handful of organizations and individuals tried to combine their knowledge with users, looking for data such as material quality and surface quality of the network, build and temperature. Some were very reluctant, because such information could also provide other insights about the process. However, with the collected data and facts new research could be formulated.

In the three (sometimes four) described / defined manifestations of Rouging it was clear that a higher alloyed Stainless steel and / or a reduction of the δ-Ferrite only had a slightly retarding effect on their formation. We also knew that all plants with temperatures above 74ºC had this problem.

In 2007, new investigations were carried out at Force Technology. They ruled out material defects and corrosion could cause an "outbreak" of Rouging. Also extensive research was carried out to find out more about the strengthen- or delaying effects of the circumstances involved. The report expressed that many more studies were needed to provide additional insights.

Conclusion and recommendations
I spoke with -in my eyes "guru" in the field of materials, I asked him why the composition of the present Stainless steel could not be changed a little. He replied "we know what the effect is of Chrome, Molybdenum and Nickel , but we have not a clue how they are working with all the other (traces of) elements ... we will need a couple of generations before we fully understand this."

We still know very little about the mechanism causing Rouging. A coloration that is stuck to the material and which complexion is dependent on temperature, flow rate and the underlying material surface ... .. Something that actually -in the form of coloured architectural sidings – is applied on buildings, but in these circumstances we simply have a lack of knowledge. Perhaps the passive oxide layer "dissolves" on the stainless steel? A layer that - if you damage it - repairs itself within 40-44 hours, just with the surrounding air.

However, if that same oxide layer is covered with water, and we imagine that in water the oxygen is 20 times less than in the air, that the amount of oxygen in water of 30ºC is reduced by 50% .... How much oxygen is left at 60 -70ºC, combined with a high flow rate and high pressure? Is that enough to maintain the passive oxide layer?

Professor Morbach – head of the investigations that led to the BN2 - has laid the foundation, allowing us to dive deeper into the matter. The fact is that he made a recommendation without any positive/negative effects on the formation of Rouging – simply as the higher amount of Rouge was not caused by the higher amount of Ferrite. A mistake anyone could have made ... .. Because -of course- you will find the most Rouge at the root penetration and in the HAZ. However, in this area the roughness is the largest and therefore the available surface material – resulting in the most discoloration. The consequence of this is that a normal amount of δ-ferrite does not have a negative effect, which in turn also makes no sense to specify the quantity.

The formation of Rouge is accelerated by:
- A temperature above the 60ºC
- A higher flow velocity
- A Metalblank material surface
- A pickled material surface
- Condensate

The formation of Rouge is delayed by;
- A Electropolished material surface
- Whenever possible, remove CO_2 (Carbon Dioxide)

Overall, the studies raise more questions than answers. Regarding the temperature we know that all with WFI systems above 72ºC have Rouging, however there are also systems where Rouge is found at a temperature of 10ºC.
One of the recommendations that I have read is to lower the temperature. A nice idea only nobody can use it ...... Therefore many things have still to be investigated.

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