Passivation

Martensitic stainless steels

What is passivation?

In presence of oxygen Cr forms spontaneously a passive protective oxide layer. Steels containing more than 12% Cr, the so-called stainless steels, passivate this way. Their passivation of takes also spontaneously place. Clean, freshly worked, is it by machining or forming, or polished or pickled surfaces do it. The chemical passivation or electrochemical polishing are technical means to activate and reinforce the passivation reaction to form still stronger, more protective oxide layers.

When is a passivation treatment recommended?

After machining or forming, a passivation treatment is recommended, independently of the steel grade.
The martensitic steels having 12 to 17%Cr forms a somewhat weaker passive oxide layer than austenitic stainless steels having a higher Cr ≥ 17% content.

Is it necessary to pickle the parts before passivation?

The pickling of the surface before passivation is recommended. It permits the elimination of all contaminations, which adhere on the surface, and metalworking chip residues. If they are not adequately pickled, dissolved or eliminated away with effectively adapted pickling solutions and processes for the job, they may impair the formation of a continuous protective passive layer. They form discontinuities in the surface oxide layer, which may become the potential sources and sites of corrosion spots. Which, in the worst case, may extend rapidly to cover the surface as a whole.

Attention! A wrong saving

The pickling operation is oft misunderstood and considered as an unnecessary cost factor only. Its omission is definitively a false saving. Which afterwards must oft be corrected with expansive reworking.

Which martensitic steels muss necessarily be pickled?

All free machining martensitic stainless steels with added S content like:

- 1.4005 - CHRONIFER® Labor 13% of L. Klein SA
- 1.4035 - CHRONIFER® Labor M-13 of L. Klein SA
- 1.4104 - CHRONIFER® Labor 17% of L. Klein SA
- 1.4197 - CHRONIFER® Labor M Plus of L. Klein SA

The totality of the S addition is present bound in MnS inclusions. The surface and volume fractions of the MnS inclusions of these steels may actually reach up to 2%.

Presence of MnS inclusions on the surface

The MnS inclusions protruding or present on the surface make the free machining martensitic stainless steels significantly less corrosion resistant and particularly pitting corrosion prone. They also create numerous surface defects and polishing problems. Their pickling away is a must.

How to eliminate the protruding MnS inclusions?

The MnS inclusions protruding on the surface of the free machining martensitic stainless steels can be dissolved, pickled away with adapted chemical solutions and processes. See page 2. These treatments are the only ways to treat these steels in order for them to exhibit an acceptable corrosion resistance.

Presence of magnetic particles on the surface

All martensitic stainless steels are ferromagnetic. In the hardened and annealed conditions they may also become hard magnetic materials. Consequently magnetic particles such as fine machining chips may adhere strongly to the surface. If they are not eliminated before the passivation treatment, they can lead to a “Flash back“ reaction in the passivation bath, staining the treated parts, suppressing their shine, and leading to expensive rework.

Modifications will not be adjusted automatically.
Last update 03/2014- 0

L. KLEIN SA • Längfeldweg 110 • P.O. Box 8358 • CH-2500 Biel/Bienne 8
Telephone 0041 (0) 32 341 73 73 • Telefax 0041 (0) 32 341 97 20 • www.kleinmetals.ch • info@kleinmetals.ch

Passivation

Martensitic stainless steels

Which are the risks?

The omission of the pickling operation may lead to “Flash back“ reaction during the passivation treatment. The resulting stained parts must be reworked, generally at high cost.
Additionally, there is still the danger that during storage and later use of the parts, a delayed resurging of the passivation solution having penetrated into the MnS cavities takes place, if they have not been properly rinsed before and after passivation. So as to be the source of potential expansive reworks and warranty issues.

Reference and link

Passivating and Electropolishing Stainless Steel Parts, John H. Magee, Carpenter Technology Corporation, 2007

Passivation Nitric acid treatment

Steel grade	Passivation treatment
Martensitic steels with 12-14% Cr	Nitric acid 20%$_{vol}$ Temperature : 49-60°C Duration : 30 min
Martensitic steels with high C	Nitric acid 20% $_{vol}$ + 22 g/L natrium dichromate Temperature : 49-60°C Duration : 30 min
Precipitation hardening martensitic steels	*or alternative* Nitric acid 50%$_{vol}$ Temperature : 49-60°C Duration : 30 min

Passivation Free machining martensitic stainless steels with added S

1. Natrium hydroxide 5%$_{weigth}$ at 71-82°C /30 min
2. Water rinsing
3. Nitric acid 20%$_{vol}$ + 22 g/L natrium dichromate at 49-60°C / 30 min
4. Water rinsing
5. Natrium hydroxide 5%$_{weigth}$ at 71-82°C /30 min
6. Water rinsing

Comparison of the nitric and citric acid processes

Examples of steels	Cr content (%)	Passivation treatments		
		Tempera-ture (°C)	Duration 30 min	Duration 30 min
Martensitic PH Precipitation hardening	11.5 à 17.5	66	20%$_{vol}$ citric acid	Nitric acid 20%$_{vol}$ + 22 g/L $Na_2Cr_2O_7$
			20%$_{vol}$ citric acid	Nitric acid 20%$_{vol}$
Martensitic	16	49–54	20%$_{vol}$ citric acid PH 5 adjusted with natriun hydroxide adition	Nitric acid 20%$_{vol}$ + 22 g/L $Na_2Cr_2O_7$
Free machining martensic (with sulfur)	≤ 13	44		*Prefered solution:* Nitric acid 20%$_{vol}$ + 22 g/L $Na_2Cr_2O_7$