



**Description:**

*Irregularities on the surface of water-cooling blocks*

**Task:**

*To find reason(s) for the damage to a water-cooling block using the appropriate methods*

**Analysis:**

The analyses were performed at the "Jožef Stefan" Institute, Advanced Materials Department. The explanation for the observed processes is given in a general manner.

Optical microscopy (Olympus BX60F, Tokyo, Japan) and scanning electron microscopy (JEOL-840A, Tokyo, Japan) were used to inspect the surface of the nickel-plated copper block for water cooling. Optical microscopy is very sensitive to surface roughness thus it is not possible to focus on all the details at different levels simultaneously. Semi-quantitative energy-dispersive spectroscopy (EDS) was employed to obtain an approximate chemical composition for the surface of the metal block.



# **Block #1**



**Block #1 used by user running distilled water and silver kill coil (1 month of use)**

An EK FC470-GTX nickel-plated copper block for the water cooling of computers exhibited a problem with the nickel-plating vanishing, thus exposing the copper underneath. The fluid used in the water-cooling system was distilled water, and a bulk silver coil was used to inhibit algae growth. The process occurred on the surfaces that are close to the plexi-glass top of the block. Additionally, a whitish deposit was formed on the surfaces of the block's chamber (Fig. 1–3).



**Figure 1: Image of the analyzed water-cooling block.**

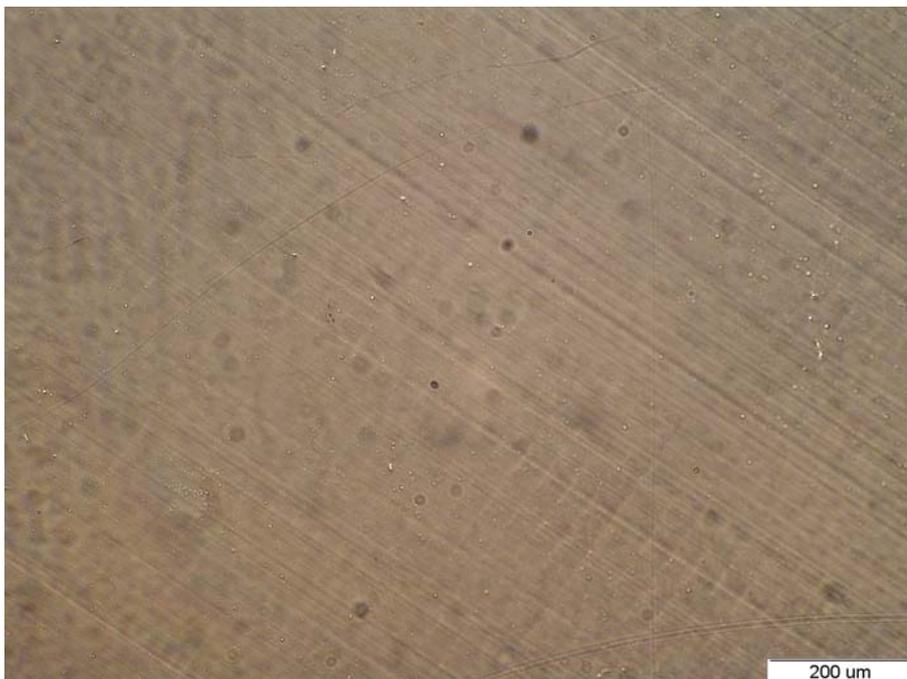


**Figure 2: Whitish deposits on the surface of the block's chamber.**

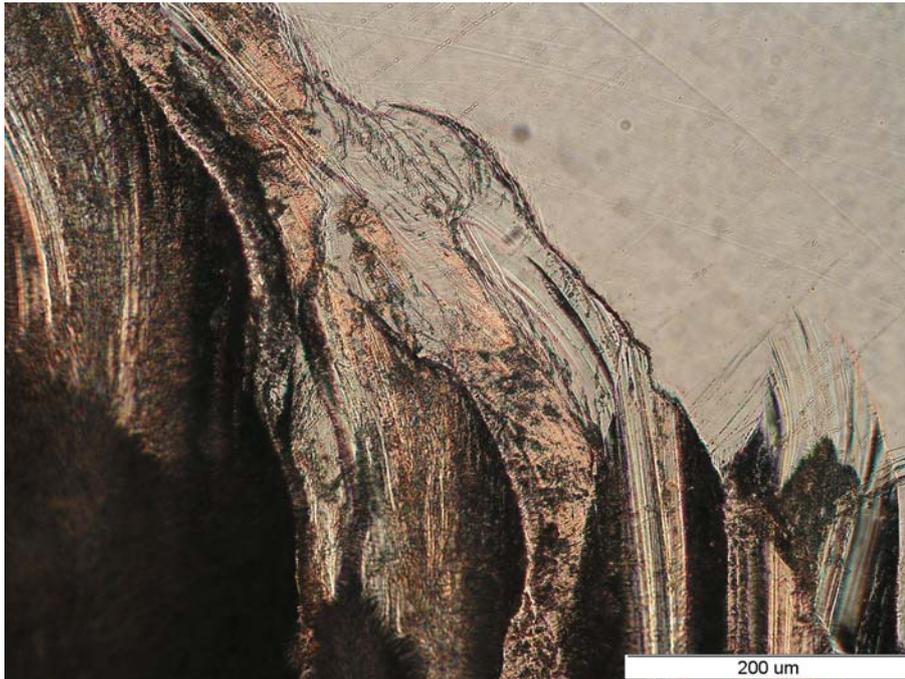


**Figure 3: Exposed copper on the surfaces close to the plexi-glass top of the block.**

First, the surface of the block that was not in contact with the cooling medium was inspected (Fig. 4). There were no visible defects in the nickel plating; the surface was completely covered with nickel. The surface roughness of the copper base was also maintained for the nickel coating. Fig. 5 shows the edge of the screw hole where the nickel coating was damaged by the screw (made by the customer). The adhesion of the nickel coating is suitable, no peeling or cracking of the coating was detected.

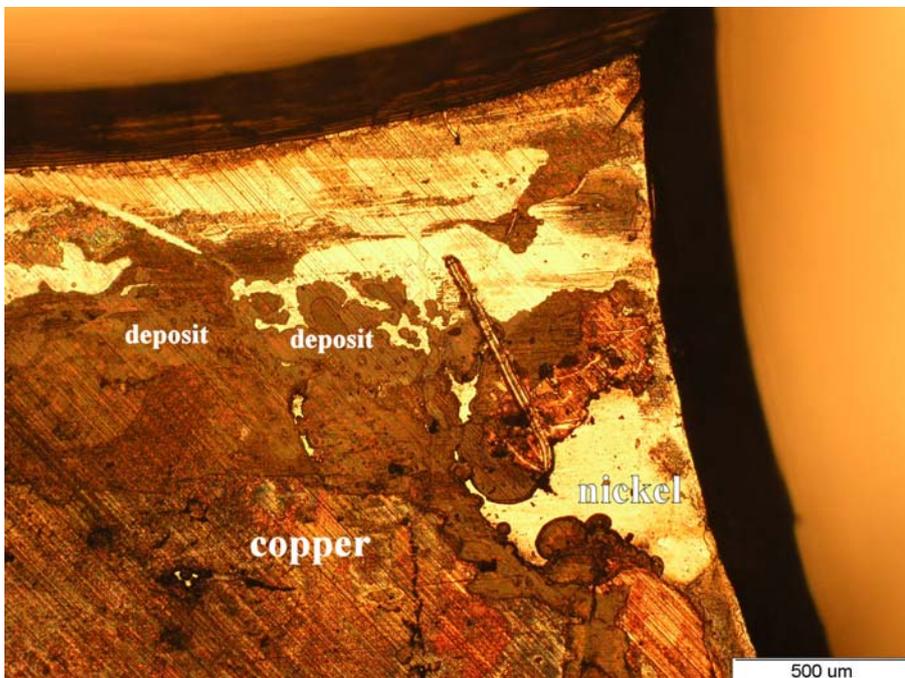


**Figure 4: Surface of the block that was not in contact with the cooling medium.**



**Figure 5: Scratches on the edge of the screw hole. The colors of the copper and nickel metals can be distinguished.**

Figs 6 and 7 show the upper surface of a cooling rib, which is close to the plexi-glass cover of the block. Besides the nickel coating (bright) and the exposed copper (red-brown color), a deposit covering part of the surface can be distinguished.



**Figure 6: Surface of a cooling rib.**

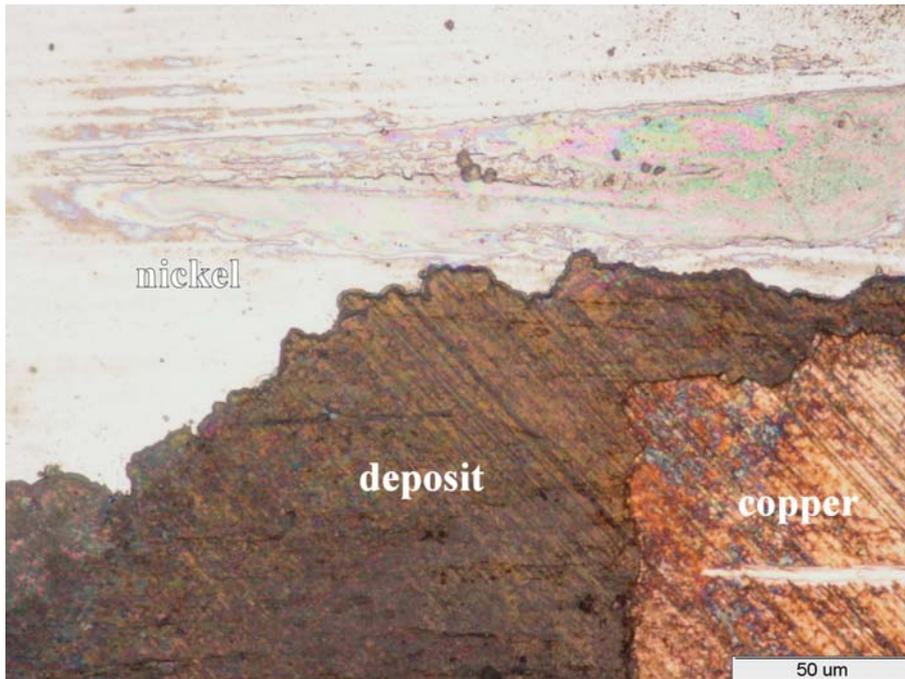


Figure 7: Surface of a cooling rib; higher magnification.

The rounded edges of the nickel/copper boundary (Fig. 8) indicate that the process behind the nickel-coating failure is corrosion. Additional evidence for the corrosion process is the gradual removal of the nickel coating by layers, seen on the nickel/copper boundary (Fig. 9). The peeling mechanism, for which straight cracks in the nickel coating are expected, is excluded.

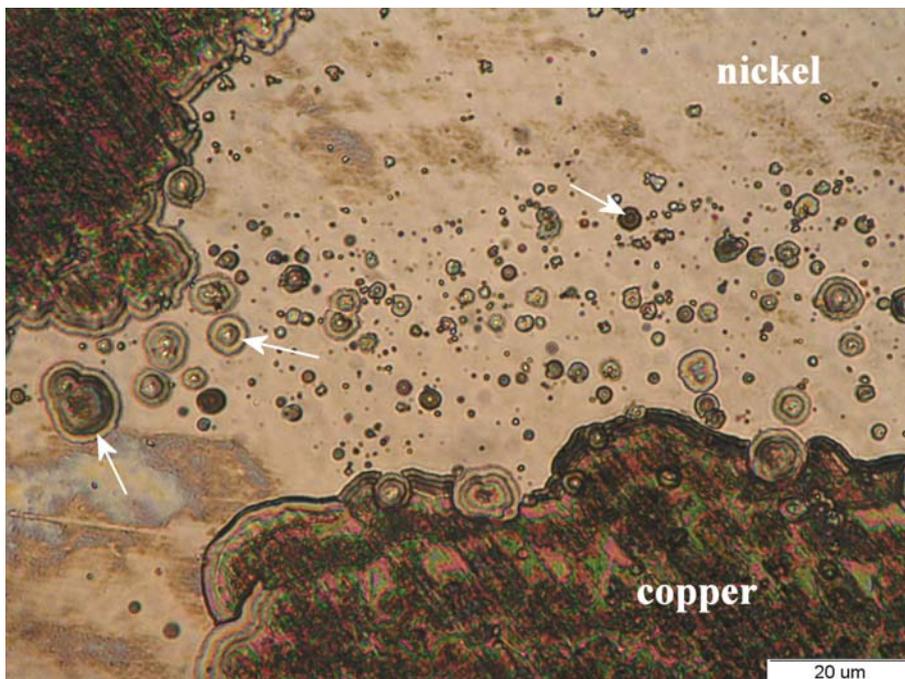


Figure 8: Corroded nickel coating and exposed copper. New corrosion holes are indicated by arrows.

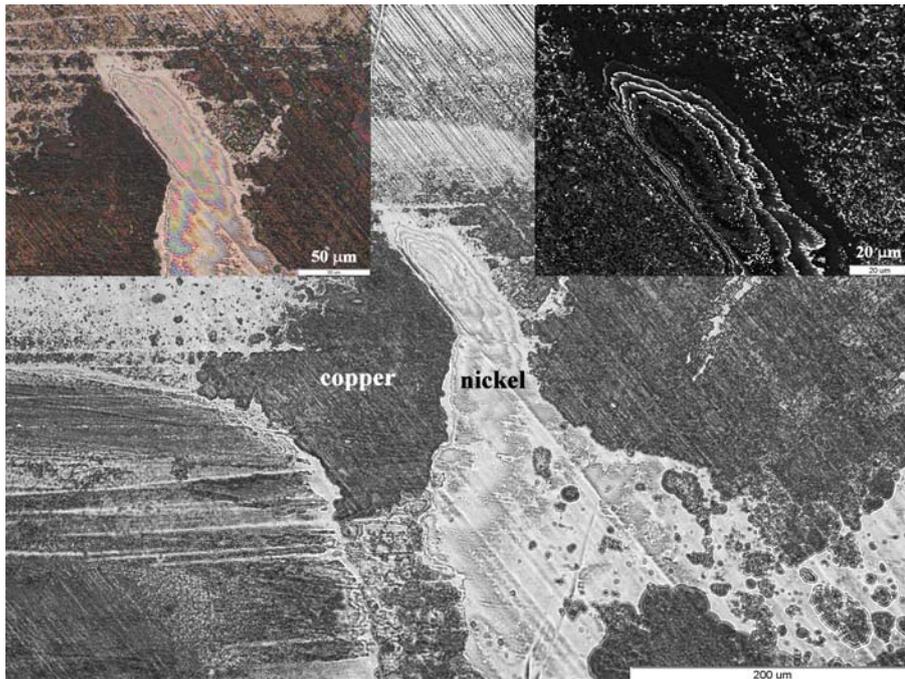


Figure 9: Island of nickel coating exhibiting gradual corrosion of the nickel layers.

The adhesion of the nickel coating near the corroded surface was checked with fine pincers. A scratch was made from the copper to the nickel (Fig. 10). No cracking of the nickel coating was observed. However, cracking of the deposit can be clearly seen in Fig. 11. Such behavior is expected, since the deposit is only physically bound (not chemically) to the surface. Straight cracks can be observed and the deposit is peeling off.

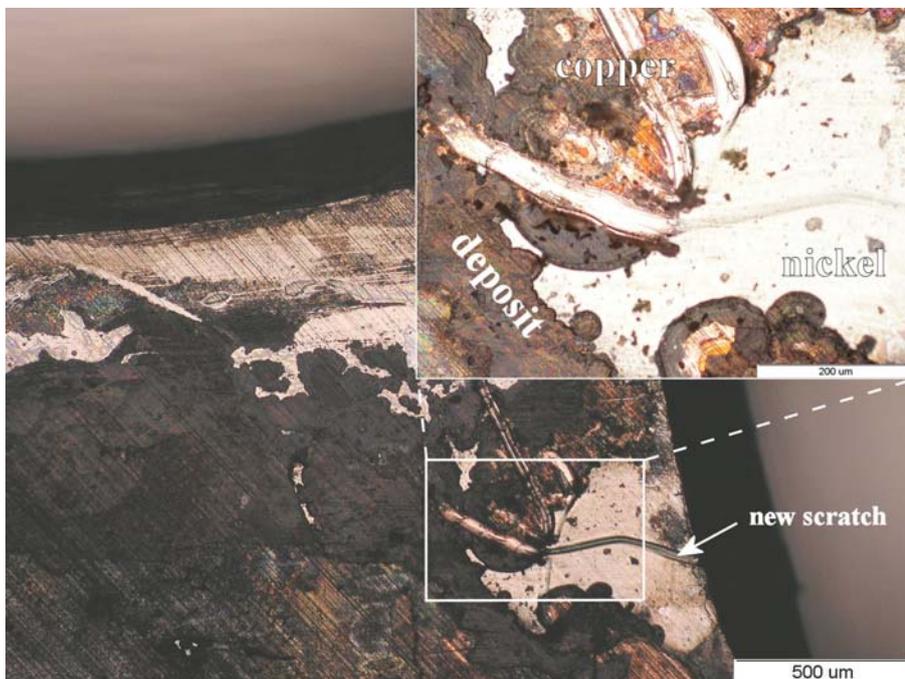


Figure 10: A scratch made by pincers (compare with Fig. 6). The scratch from copper to nickel is continuous and no cracking is observed.

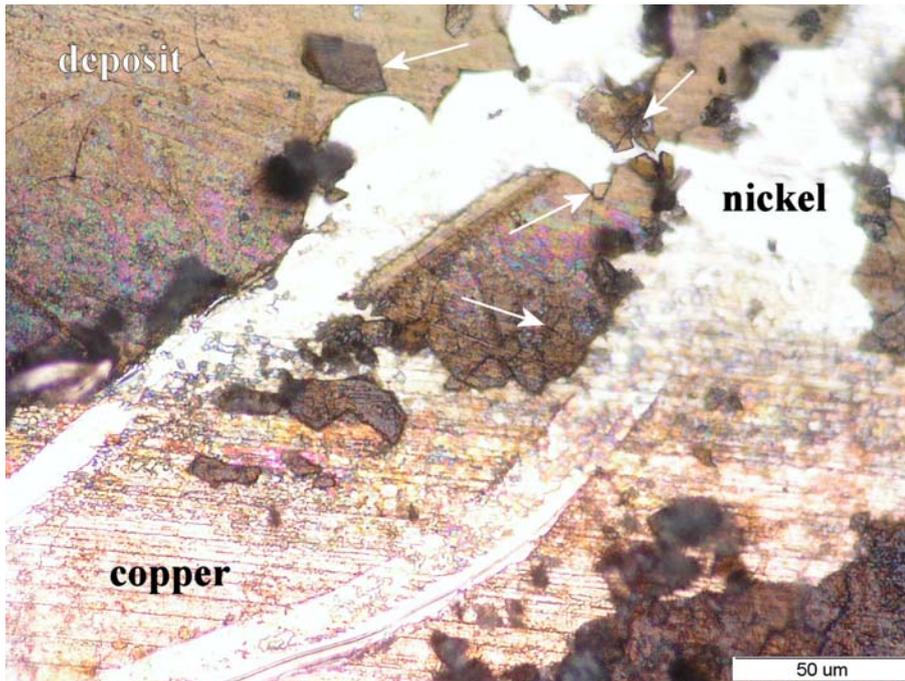


Figure 11: Cracking of the deposit around the pincers' scratch. Some cracks and straight edges are marked by arrows.

White deposits in the chamber of the water-cooling block are shown in Fig. 12. Small corrosion holes are also visible, indicating that the corrosion process is accelerating and spreading to the less-exposed surfaces. Such behavior is expected due to the higher conductivity of the fluid, since the concentration of the dissolved ions in the closed water-cooling system increases.

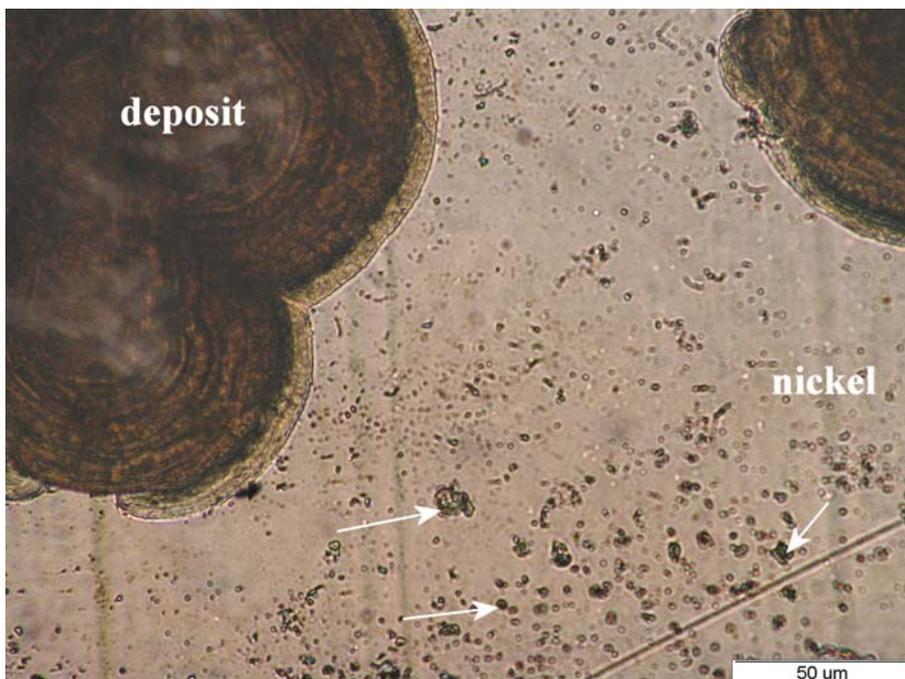


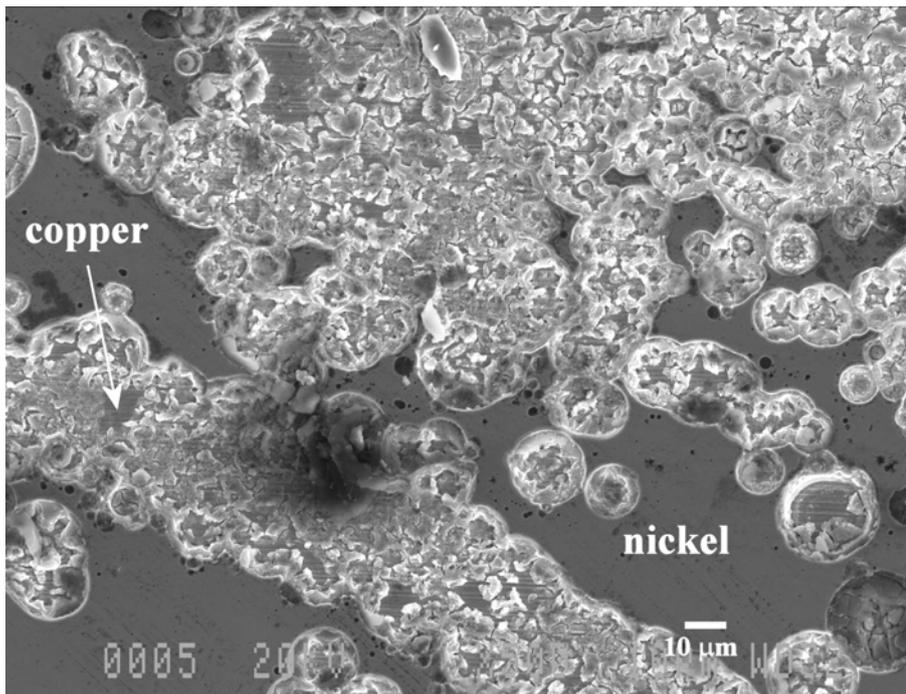
Figure 12: White deposits on the nickel coating in the chamber of the water-cooling block. Corrosion holes are indicated by arrows.



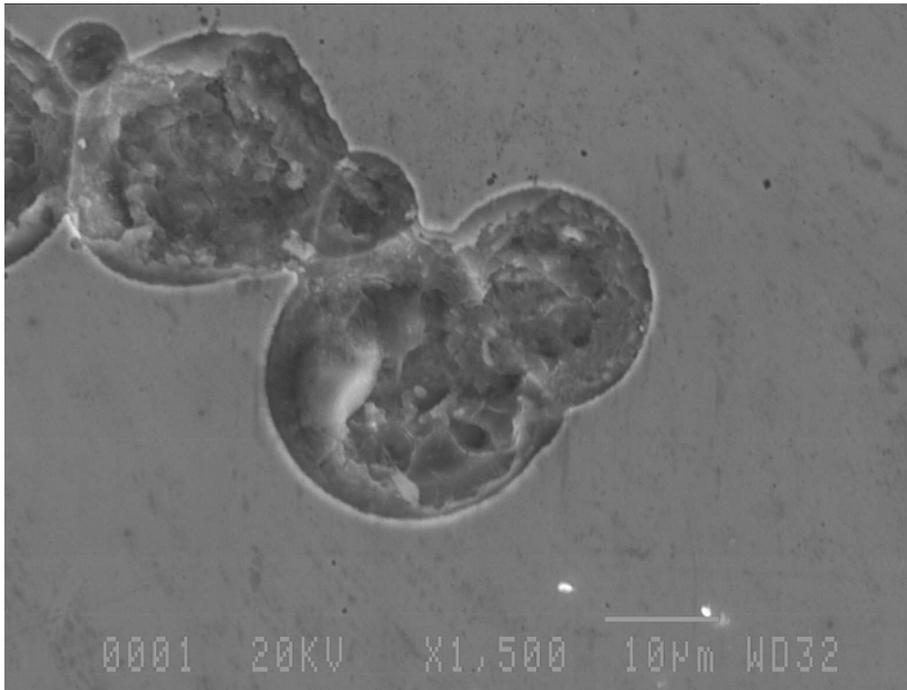
*Scanning electron microscopy*

The corroded part of the water-cooling block (a cooling rib) was cut out and investigated with scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The latter technique gives information about the chemical composition of the upper few  $\mu\text{m}$  of the surface.

A heavily corroded nickel-coated surface can be seen in Fig. 13. The rounded holes indicate the corrosion process. Within the corrosion holes, the small remaining particles of the nickel coating are losing adhesion with the copper surface. A higher-magnification image of a corrosion hole is shown in Fig. 14.

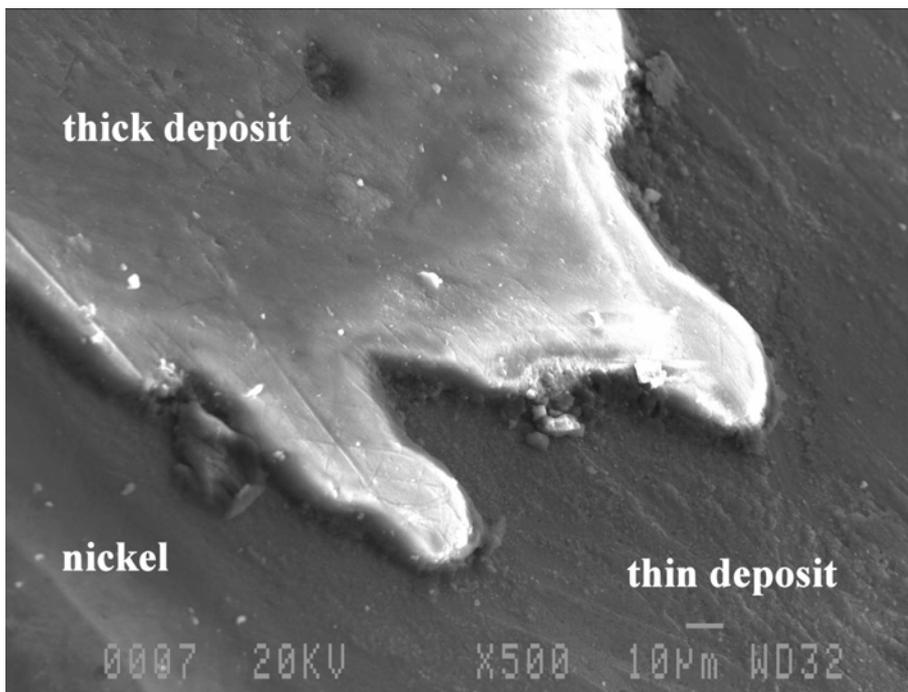


**Figure 13: Heavily corroded nickel coating.**



**Figure 14: Corrosion hole.**

Thick deposits were observed, especially near the edge of the cooling rig (Fig. 15).



**Figure 15: Deposits on the nickel coating.**

The deposit on the nickel coating in the chamber of the block is shown in Fig. 16. The bright color of the deposit indicates that it is not conductive (oxidized metal(s)). The surface roughness of the machined copper is clearly seen on the nickel coating. The small dots (marked by a circle) on the nickel are the very beginning of the deposits (Fig. 17).

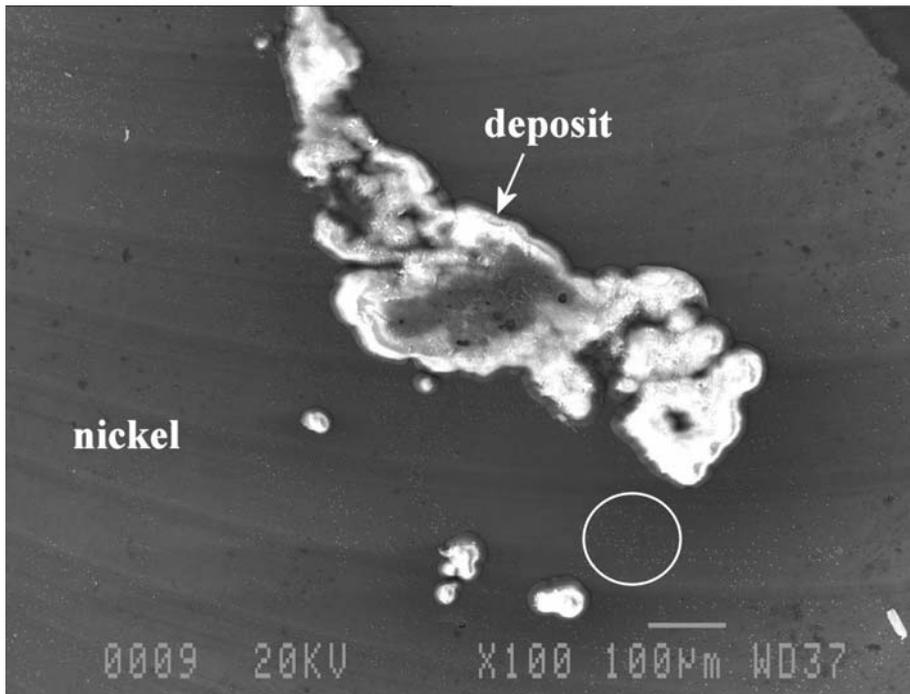


Figure 16: Deposits on the nickel coating in the chamber of the block.

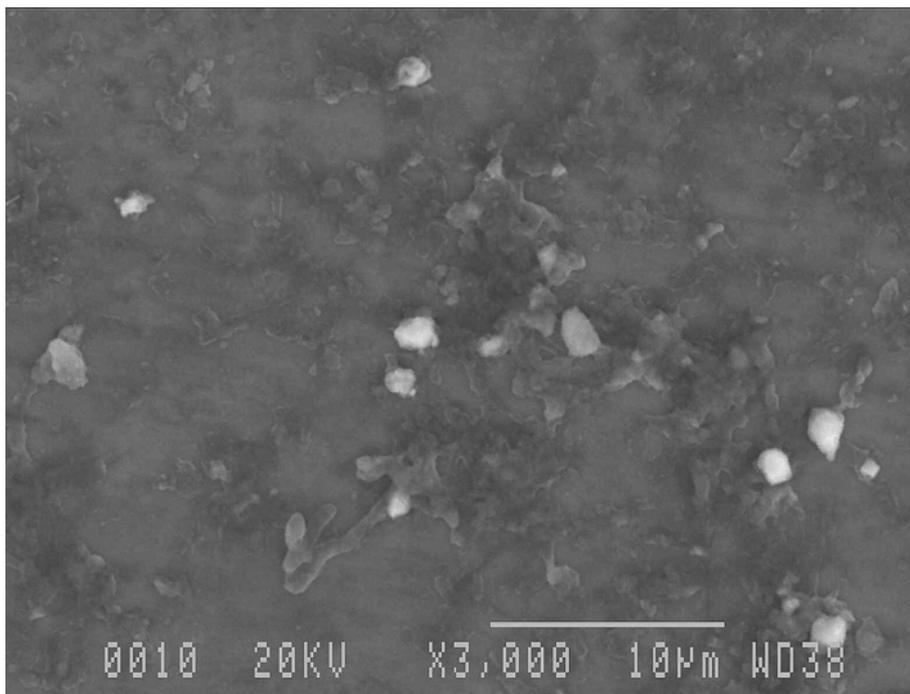


Figure 17: Origins of the deposits (higher magnification of the dots in the circle marked in Fig. 16).

The EDS analysis revealed the approximate chemical composition of the analyzed surfaces. The nickel coating consists of pure nickel (Ni) metal (Fig. 18). No oxygen was detected in the coating, while the copper (Cu) signal comes from the underlying base material. Also for the exposed copper the EDS results show pure copper metal (Fig. 19).

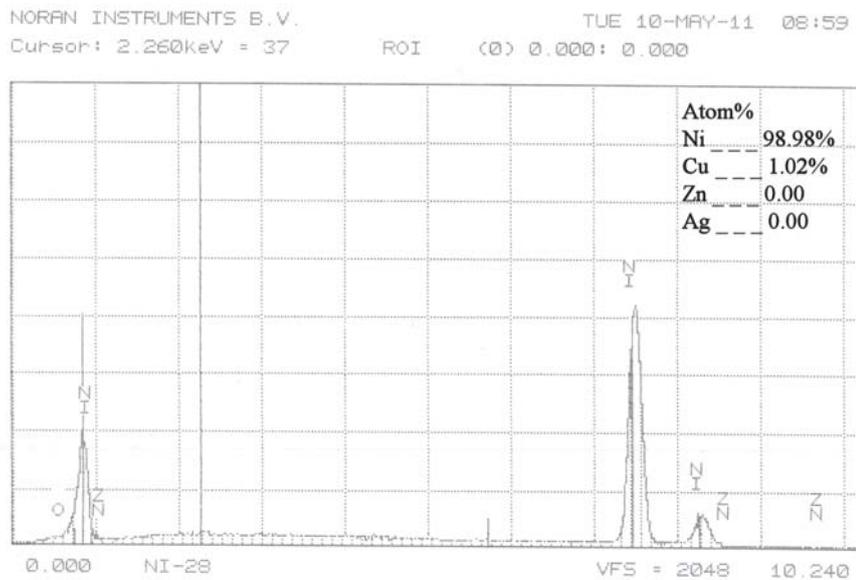


Figure 18: Typical EDS spectrum of a nickel metal coating.

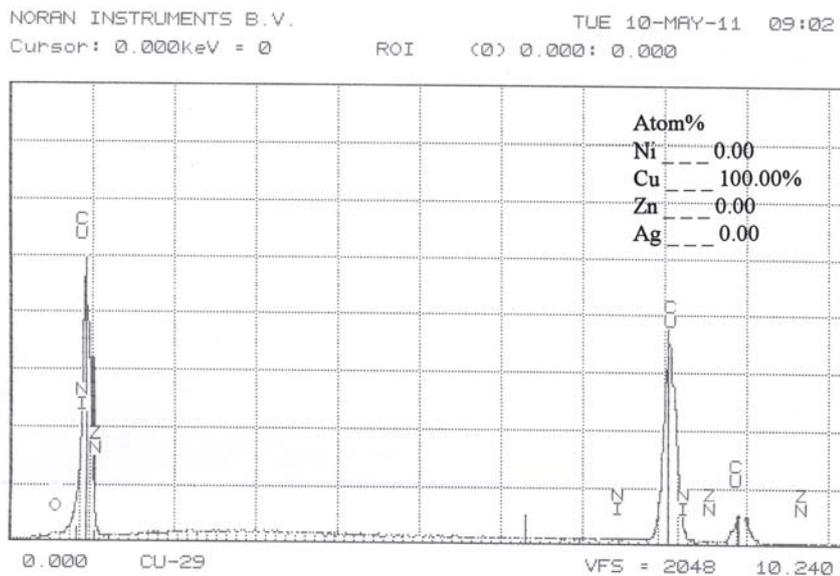


Figure 19: Typical EDS spectrum of a copper metal base.

The chemical composition of the deposits is more complex as well as inhomogeneous. Zinc (Zn) is the major constituent of the deposits and it is found in the oxidized form (ZnO), as is clear from Fig. 20. However, additional elements like sulfur (S), silicon (Si), barium (Ba) and silver (Ag) were detected on different spots of the deposits (Fig. 21). The concentration of silver is at the limit of detection. There are additional elements in the deposits; however, their concentration is too low for a proper identification.

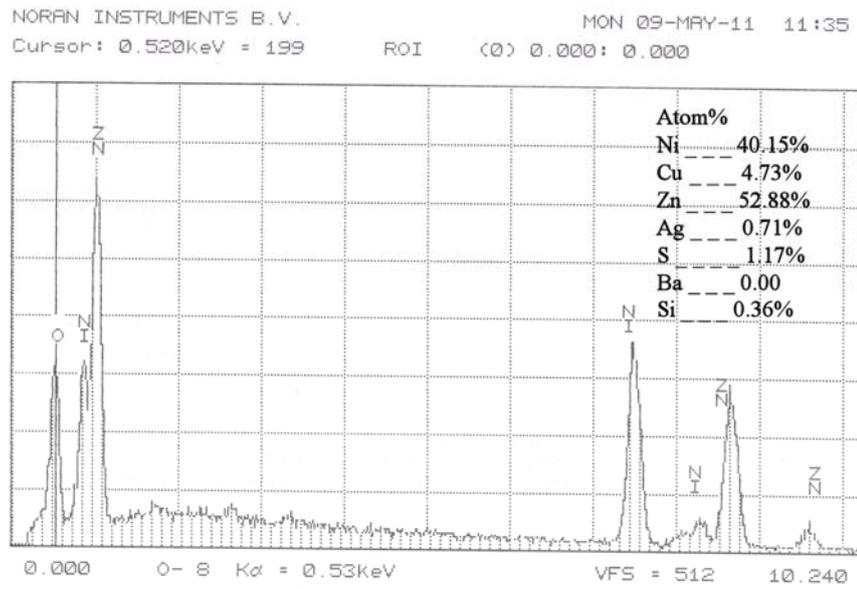


Figure 20: EDS spectrum of deposits.

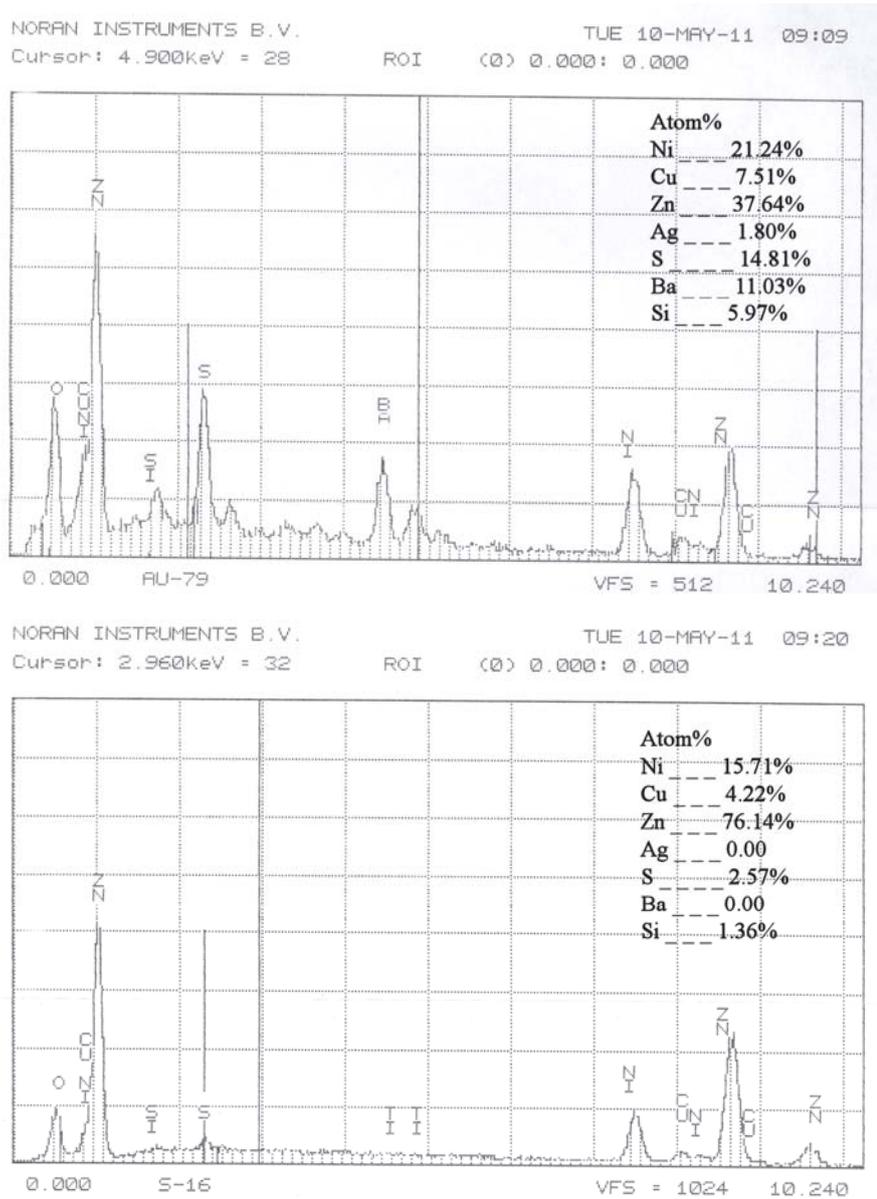


Figure 21: EDS spectra of deposits.



### Explanation:

The problem with the nickel coating occurred due to corrosion of the nickel plating. Peeling of the nickel coating due to unsuitable adhesion to the copper base was excluded. Since, besides plexi-glass, the water-cooling block consists of nickel-plated copper only (other parts like screws are separated by washers), the other elements have entered the water-cooling block from the rest of the system. A significant amount of the deposits of an external origin found on the surface of the water-cooling block indicates that the rest of the system has also suffered a rapid rate of corrosion. The other metallic parts of the water-cooling system are the pump, radiator, silver coil, etc.

First, the most likely origin of the detected elements in the deposits needs to be discussed. The major constituent of the deposits is Zn, in oxidized form ( $Zn^{2+}$ ), which probably originates from the radiator. The radiators are usually made of brass, the chemical composition of which is a copper/zinc alloy, although some minor additives are added like lead (Pb) or silicon. Silicon could come into the solution either from brass (if it is used as additive) or from grease, which is sometimes used for sticking and waterproofing of different water-cooling system parts. Different barium compounds like Ba-acetates, Ba-chloride or Ba-sulfate, are used in dyes, pigments, paints and lubricating oils. There is no idea as to how exactly the barium has come into the cooling fluid. The same can be said for sulfur; however, it could be some remains, stuck on a radiator after the manufacturing/cleaning process. Silver, the content of which is at the limit of the detection, could come from the silver coil used to inhibit algae growth. Silver ions which are dissolved from the coil are extremely toxic for bacteria and algae, and thus are also efficient in a very small concentration (silver metal is practically insoluble).

There are different types of corrosion; however, always when different metals are in contact in an electrolyte (conducting liquid) there is a danger of a galvanic corrosion. The driving force for the corrosion is the difference in the electrical potential between the different metals. The larger the potential difference, the greater the probability of a galvanic corrosion. In this process, deterioration of the less "noble" metal occurs as the more noble metal acts as cathodic and is thus protected. The values of the standard electrode potentials for the metals in question are given in Table 1. In the metal series given in Table 1, the most noble metal is silver (Ag), which acts as cathode in redox reactions with all other metals. In contrast, barium is the less noble metal and will be the first to oxidize. From Table 1, the electrode potential of a copper-nickel galvanic couple is 0.6 V under standard conditions.

**Table: Standard electrode potentials ( $E^\circ$ ) in volts (V) relative to the standard hydrogen electrode.**

Half-reaction	$E^\circ$ (V)
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	-2.9
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	-0.76
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	-0.26
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.80



Galvanic corrosion occurs in a galvanic cell, where it is employed as a source of electrical energy (Fig. 22). In a copper-zinc galvanic cell (Daniell cell) zinc metal is being oxidized and dissolved into the electrolyte. The released electrons move through the wire to the copper cathode, where they are used to reduce the copper ions, which are thus being deposited as metal copper. The flow of electrons through the connection of the electrodes produces electrical energy. To preserve the electro-neutrality, anions in the electrolyte flow in the opposite direction to the electrons. Galvanic corrosion also occurs on a single piece of metal as different parts of a metal can serve as anodes and cathodes.

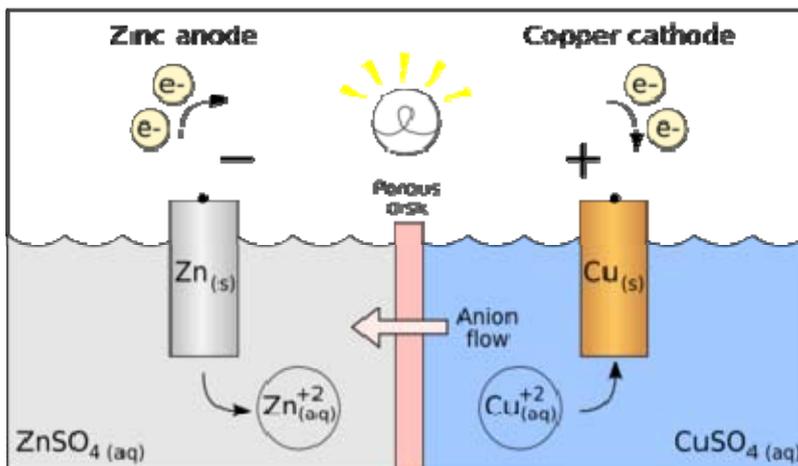


Figure: Galvanic cell with copper cathode and zinc anode.

For galvanic corrosion to occur, three conditions must be present: two dissimilar metals (or surfaces of the same metal with dissimilar potentials), a metal (conducting) path between the dissimilar metals and an electrolyte (water with any type of salt or salts dissolved in it). If one presumes that the first two conditions are satisfied, the absence of an electrolyte should prevent the corrosion processes. The use of pure, deionized water or distilled water should be sufficient, despite the fact that  $\text{CO}_2$  from the atmosphere dissolves in water, which results in its slight acidity (pH~5.5). However, when any type of ion is dissolved in deionized water, it becomes conductive and thus serves as the electrolyte. Moreover, as the water-cooling loop is closed, the concentration of ions gradually increases, which increases the speed of the corrosion.

In a water cooling system, the metal block is isolated from other metal parts of the system (it is not in direct contact with other metal parts). Thereafter, galvanic corrosion between different metal parts of the system is not possible. However, when the cooling liquid is conductive and different ions are dissolved in it, a different type of corrosion can occur.

Crevice corrosion is a localized form of corrosion, usually associated with a stagnant solution on the micro-environmental level. Such stagnant microenvironments tend to occur in crevices (shielded areas) such as those formed under gaskets, washers, insulation material, surface deposits, threads, etc. Due to a stagnant fluid with different concentrations of dissolved ions, oxygen or different acidity compared to the rest of the system, a local chemistry within the crevice can strongly deviate from the conditions in the system. In such an environment corrosion can occur or is strongly accelerated.

Regarding the investigated nickel-plated copper block, the first signs of changes were detected on the surfaces close to the plexi-glass top of the block. In these areas the water is stagnant and the dissolved ions can be concentrated and deposited, leading to a different concentration of oxygen or acids. First, only deposits of different colors were observed. Such



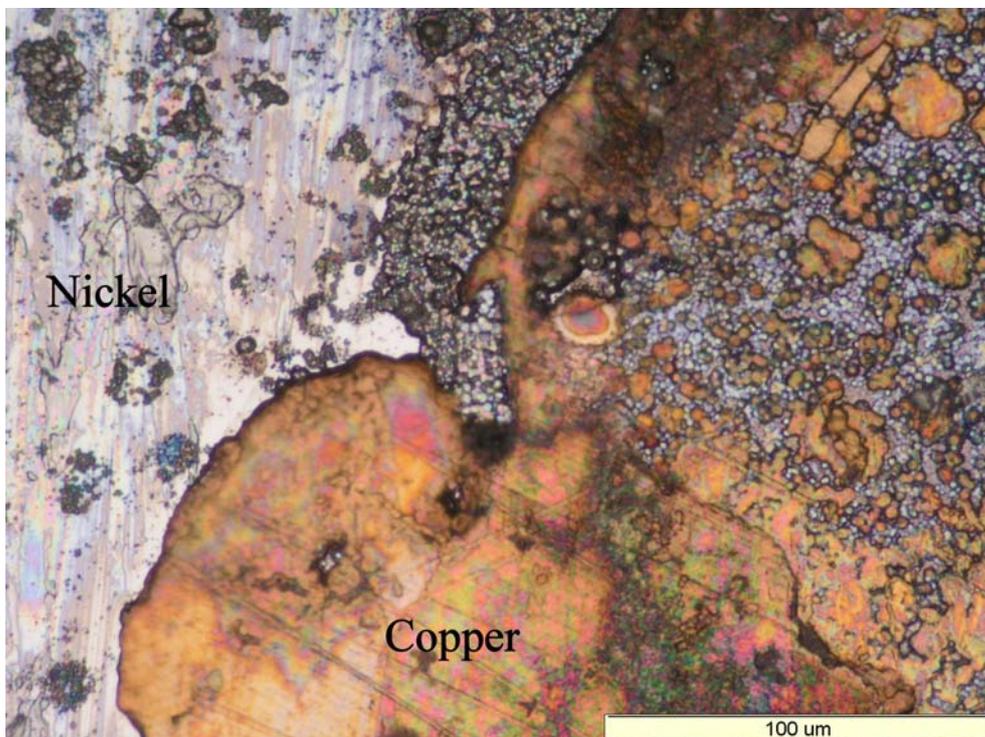
behavior could indicate crevice corrosion due to a locally changed chemistry. Subsequently, the nickel coating completely vanished and the copper metal with its distinctive color was observed. Once the copper is exposed all the conditions for galvanic corrosion between the copper and the nickel are fulfilled, and moreover, the overall corrosion process is strongly accelerated.

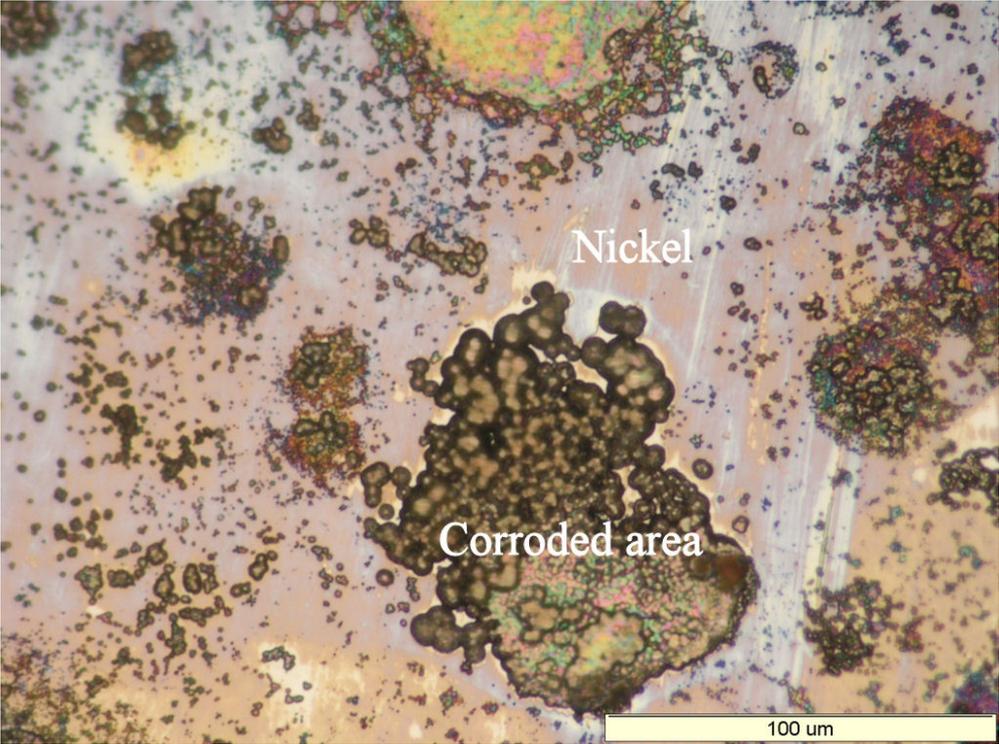
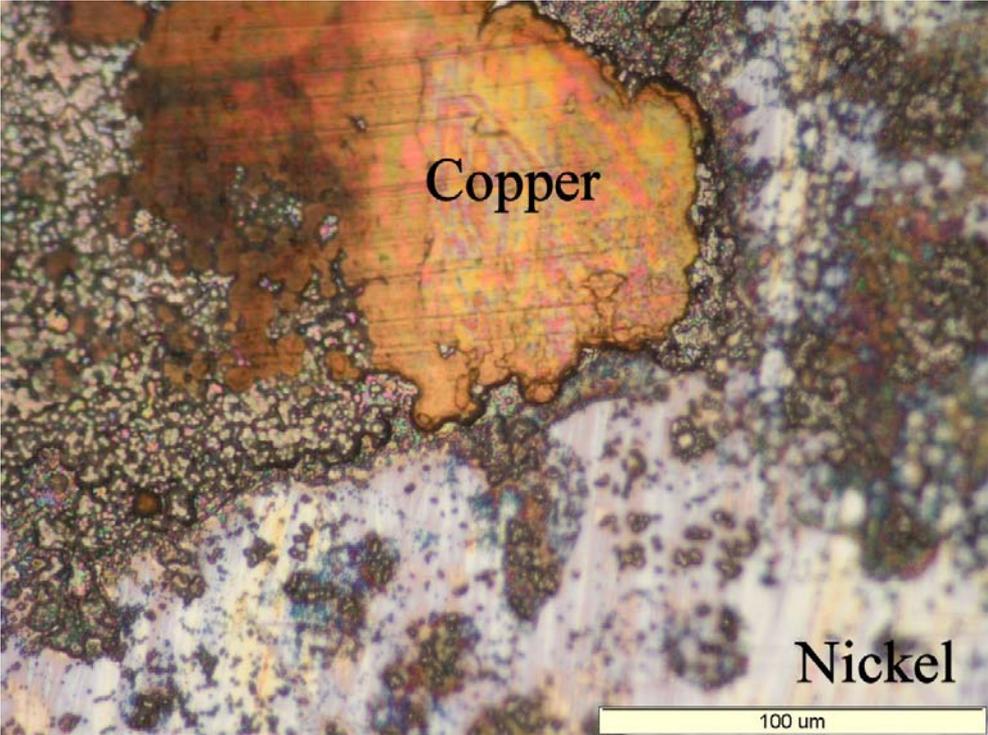


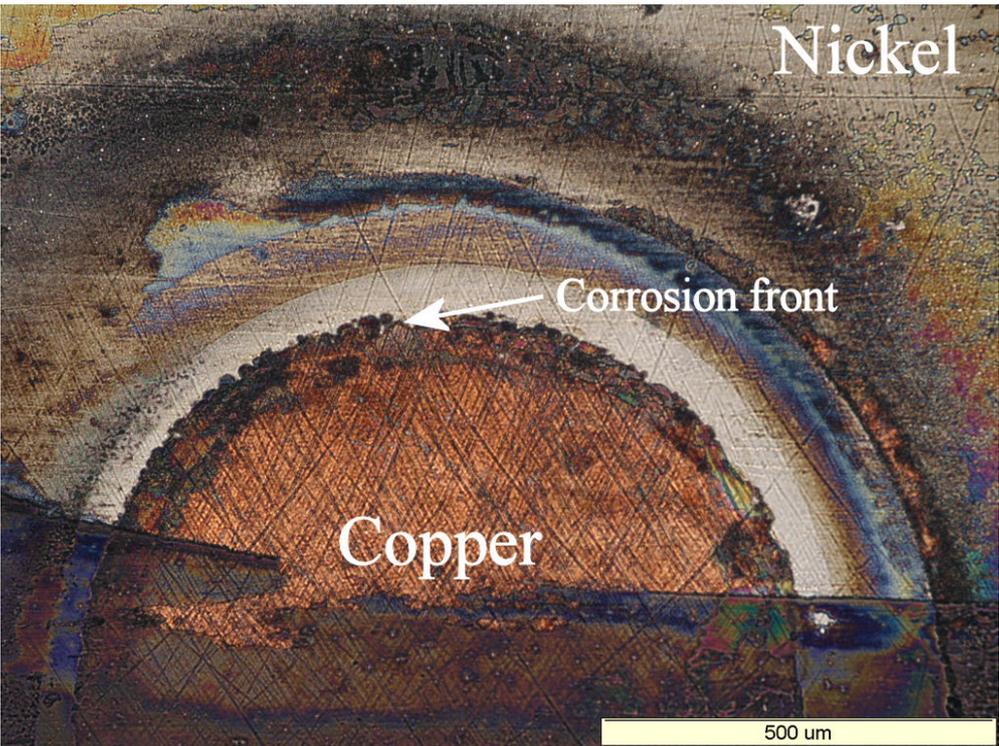
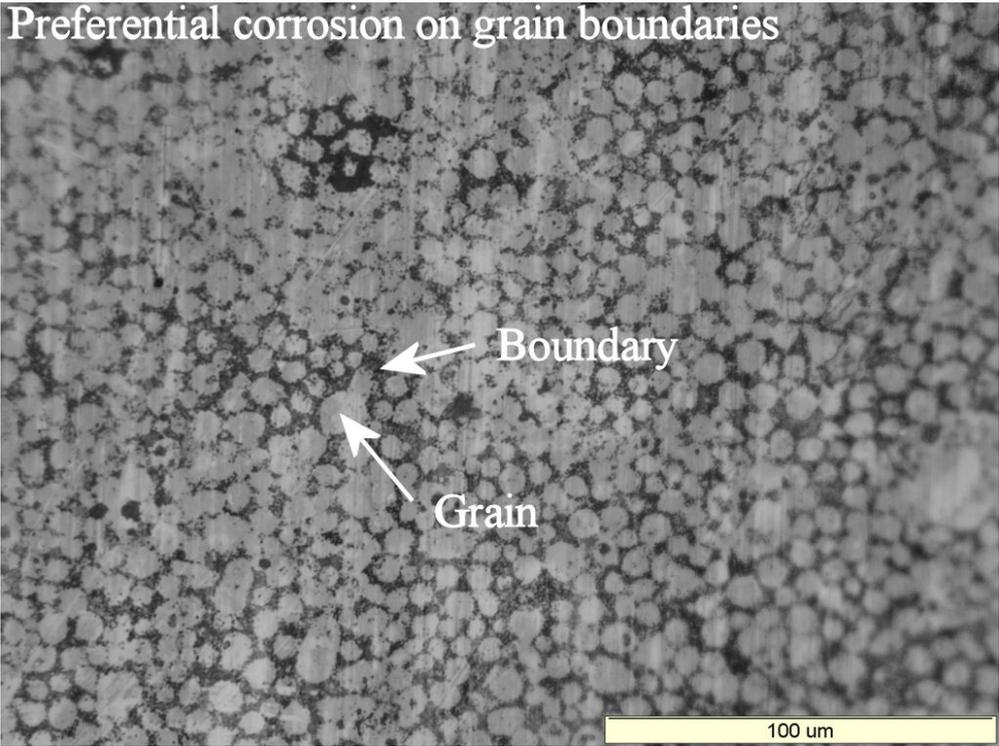
## **Block #2**

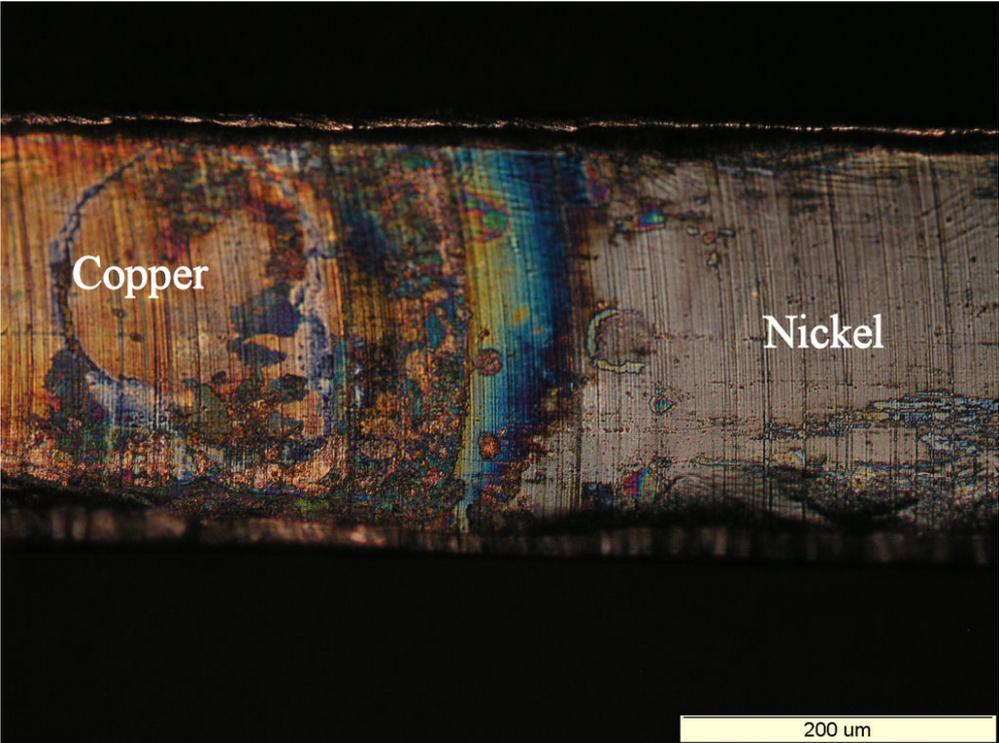
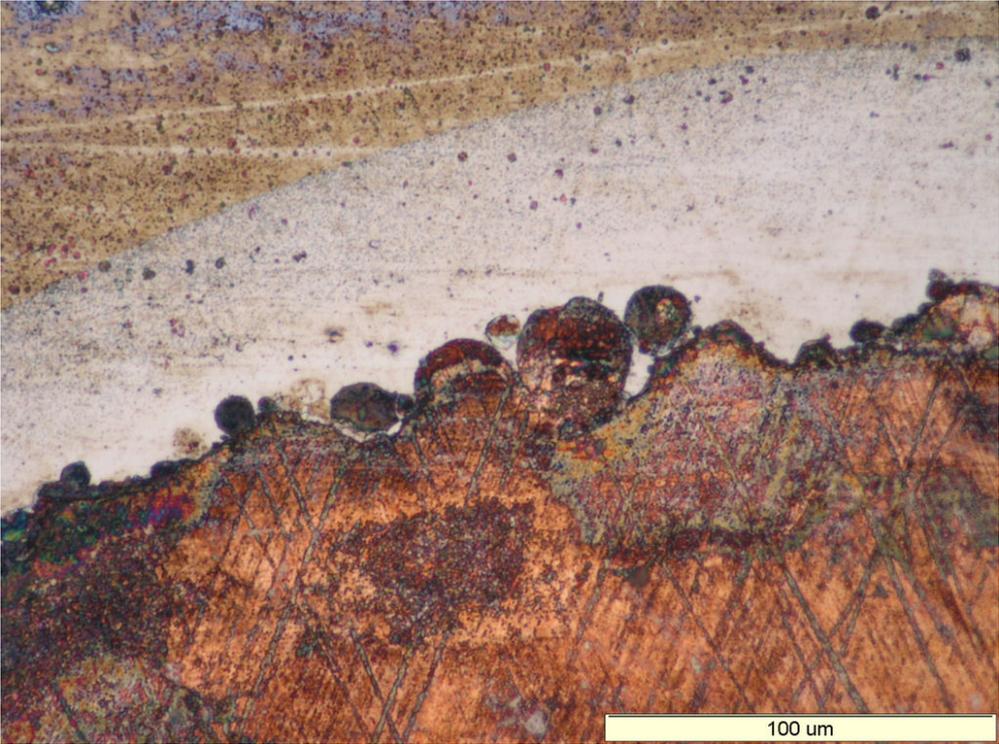


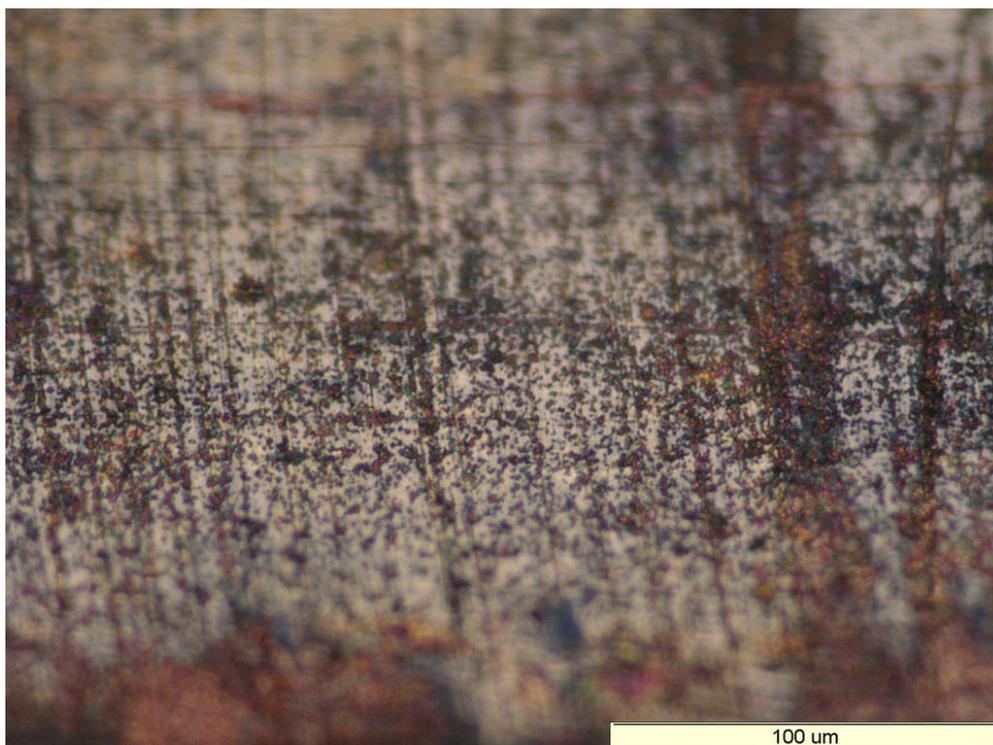
On this nickel-plated, copper, water-cooling block the surface is highly corroded. However, no peeling was detected, indicating good adhesion of the nickel coating. Different ways and progress of the corrosion are visible on different surfaces of the block; preferential corrosion starting at the grain boundaries, and semi-circle corrosion. This is due to different liquid velocities in different parts of the block. Selective corrosion occurred at a place with high a liquid velocity, while a semi-circle was produced by stagnant liquid propagating under the contact of nickel and plexi-glass cover.









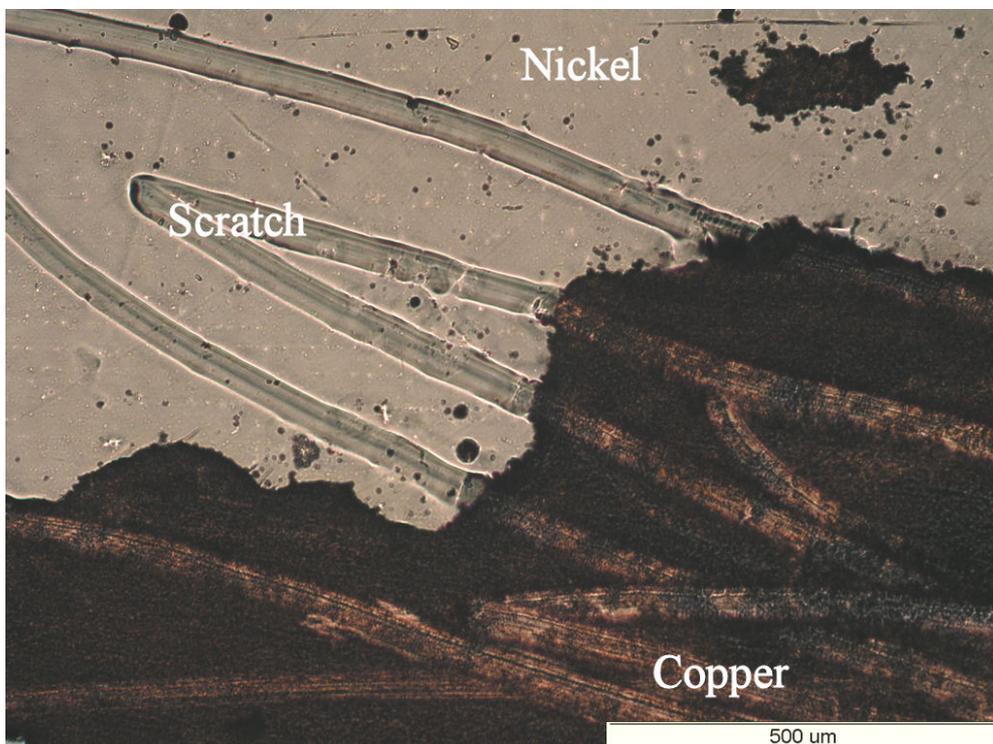


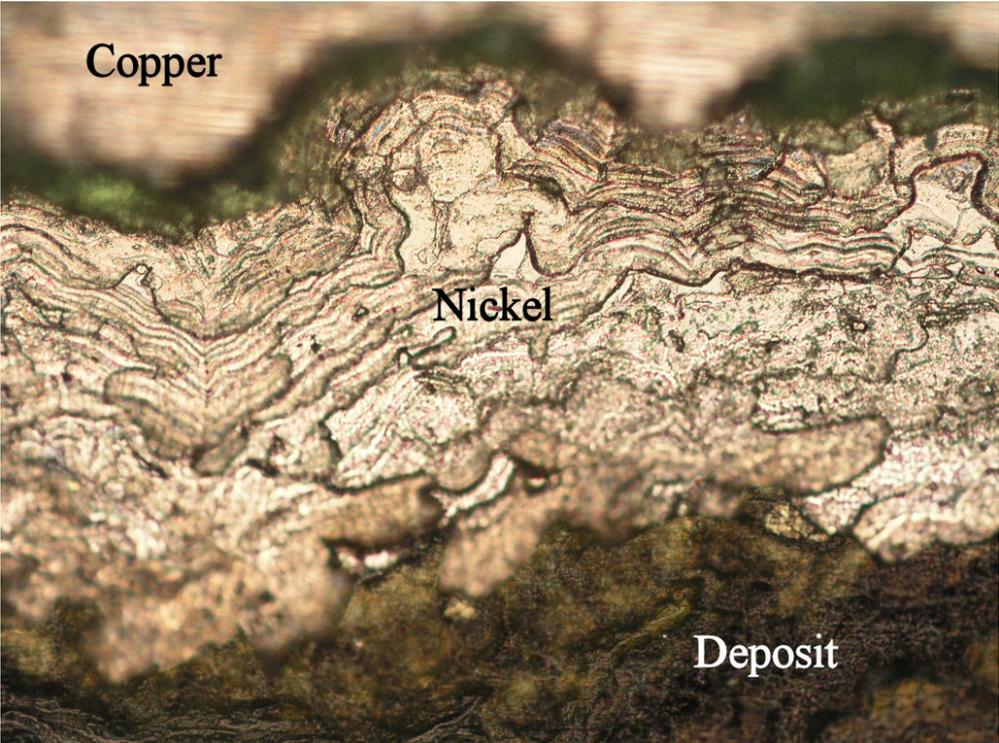


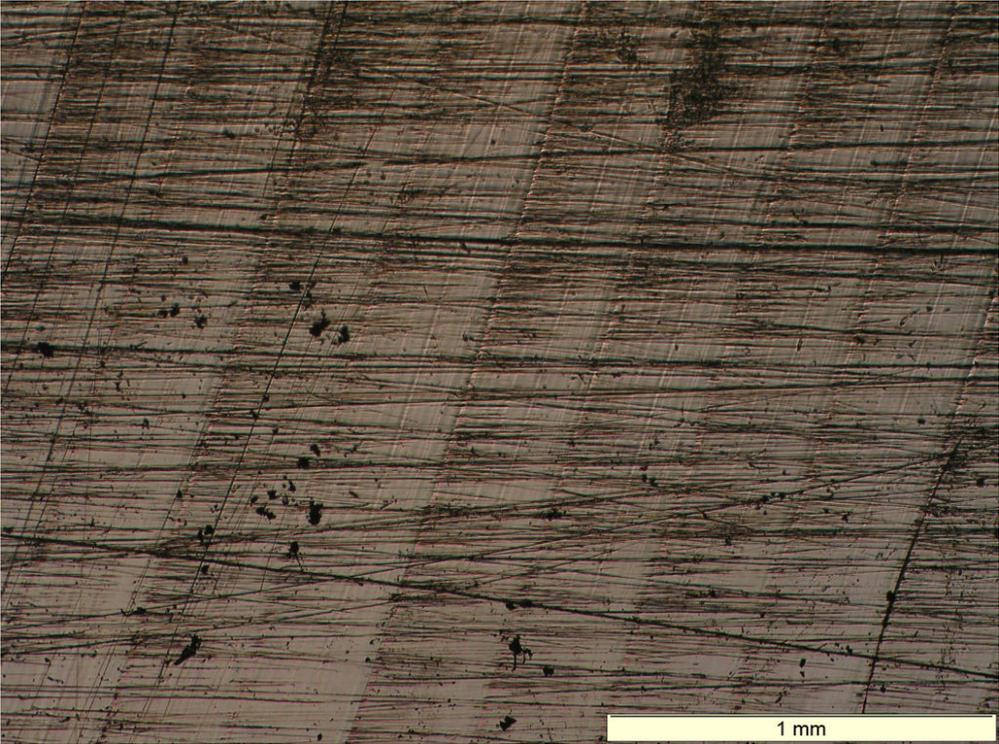
## **Block #3**



In this case there is a highly corroded nickel coating over the whole exposed surface. No peeling was detected, even on the corrosion front line. Pincers' scratches were made to test the adhesion of the coating. In contrast to the above case, a green coloration of the oxidized copper is visible. Such behavior indicates acidity of the cooling liquid, since in a non-acidic medium the copper is protected from oxidation because it is cathodic. The last figure shows scratches on an unexposed surface of the block, indicating cleaning with an abrasive medium.





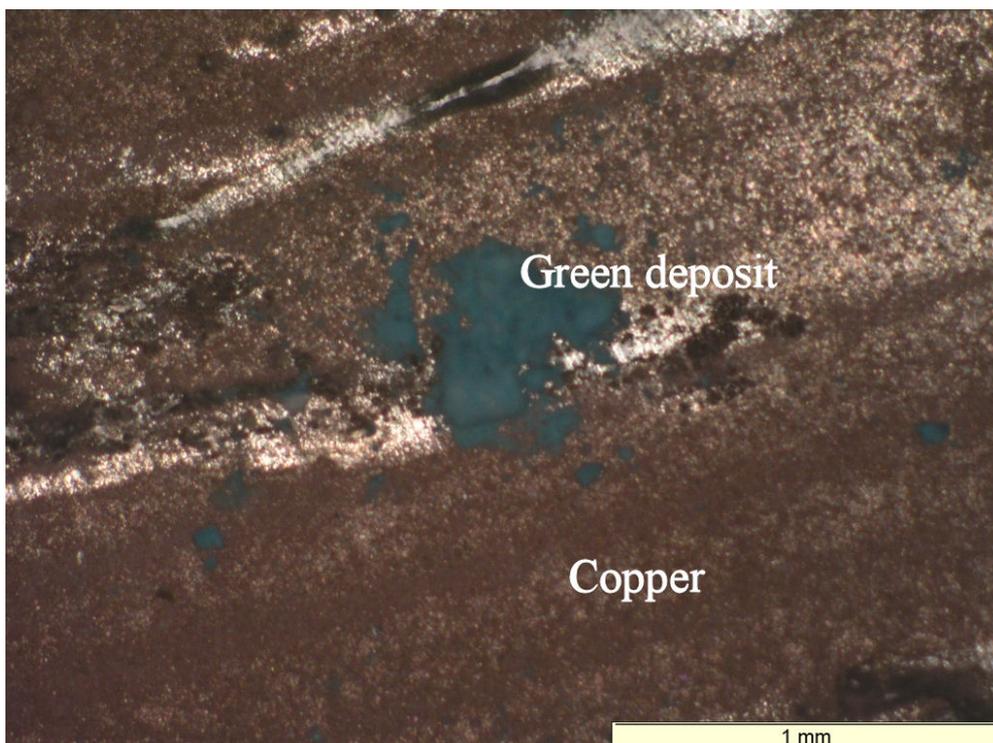


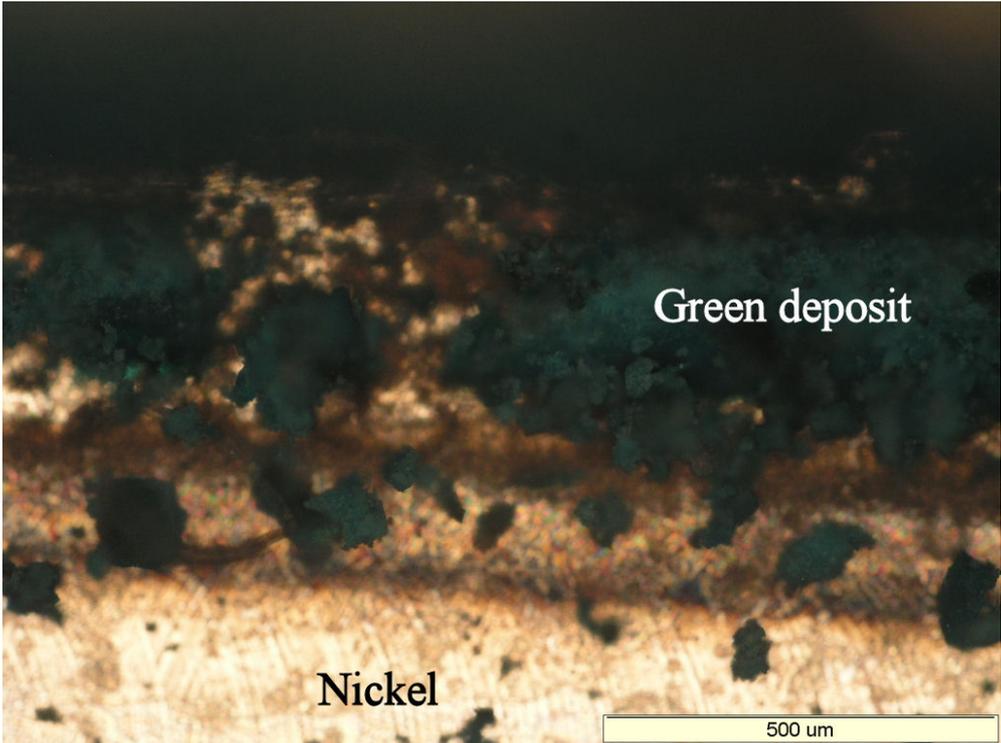
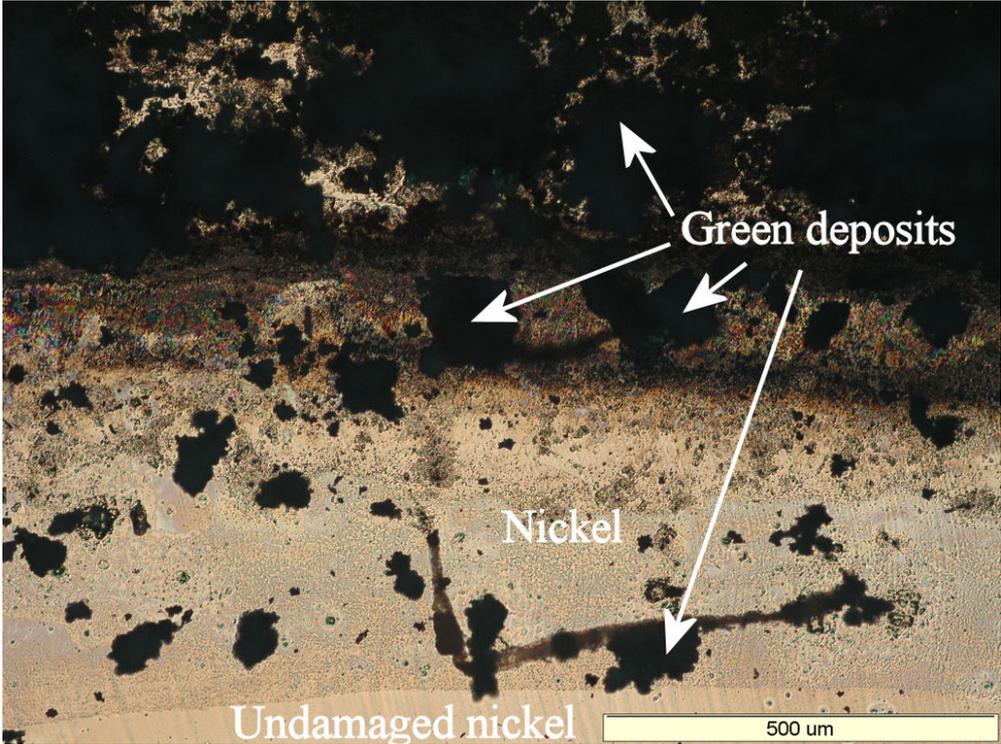


## **Block #4**



Almost all of the nickel coating was removed from the surfaces exposed to the cooling liquid. The green deposits indicate oxidation of the exposed copper due to the acidic environment. The nickel coating behind the sealing is undamaged.







## **Block #5**



**Test in controlled conditions:**

**The influence of Copper(II) sulfate pentahydrate on a Nickel-Plated copper water-cooling block**

**Goal:** To see the influence of Copper(II) sulfate pentahydrate on a Nickel-Plated copper water-cooling block. The system was tested at EKWB d.o.o. and analyzed at "Jožef Stefan" Institute, Advanced Materials Department.

Date: April 6<sup>th</sup>

Assemble the water cooling system, which consisted of:

- EK-FB R3-Genie nickel-plated water-cooling block (nickel-plated copper, acrylic top)
- EK-DCP 2.2 pump
- EK-Coolstream XT 360 radiator (material Copper fins, brass channels and chambers, tin)
- EK-10mm short fittings (Nickel-plated brass)
- Masterkleer 10/13 PVC tubing

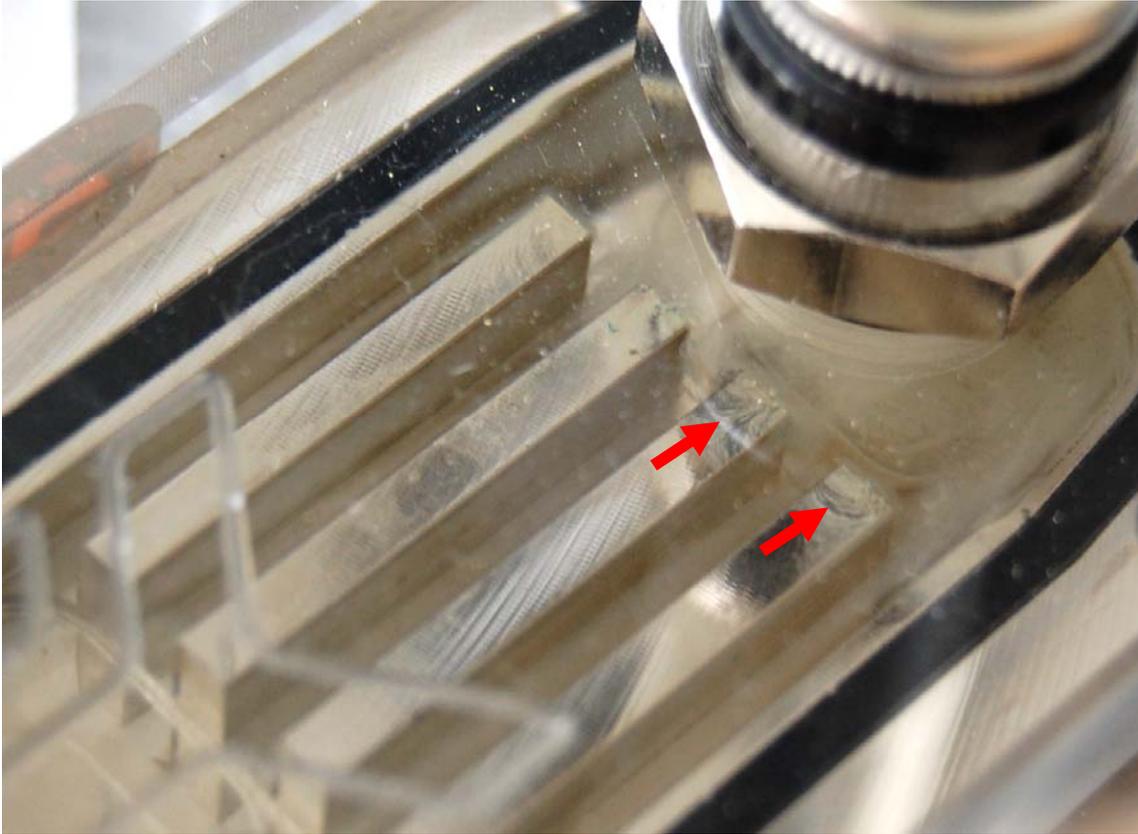
Coolant:

- Distilled water
- 5 mL of Copper(II) sulfate pentahydrate 4.1% (high concentration to accelerate the process)

Date: April 28<sup>th</sup>

Observation: First look at nickel corrosion

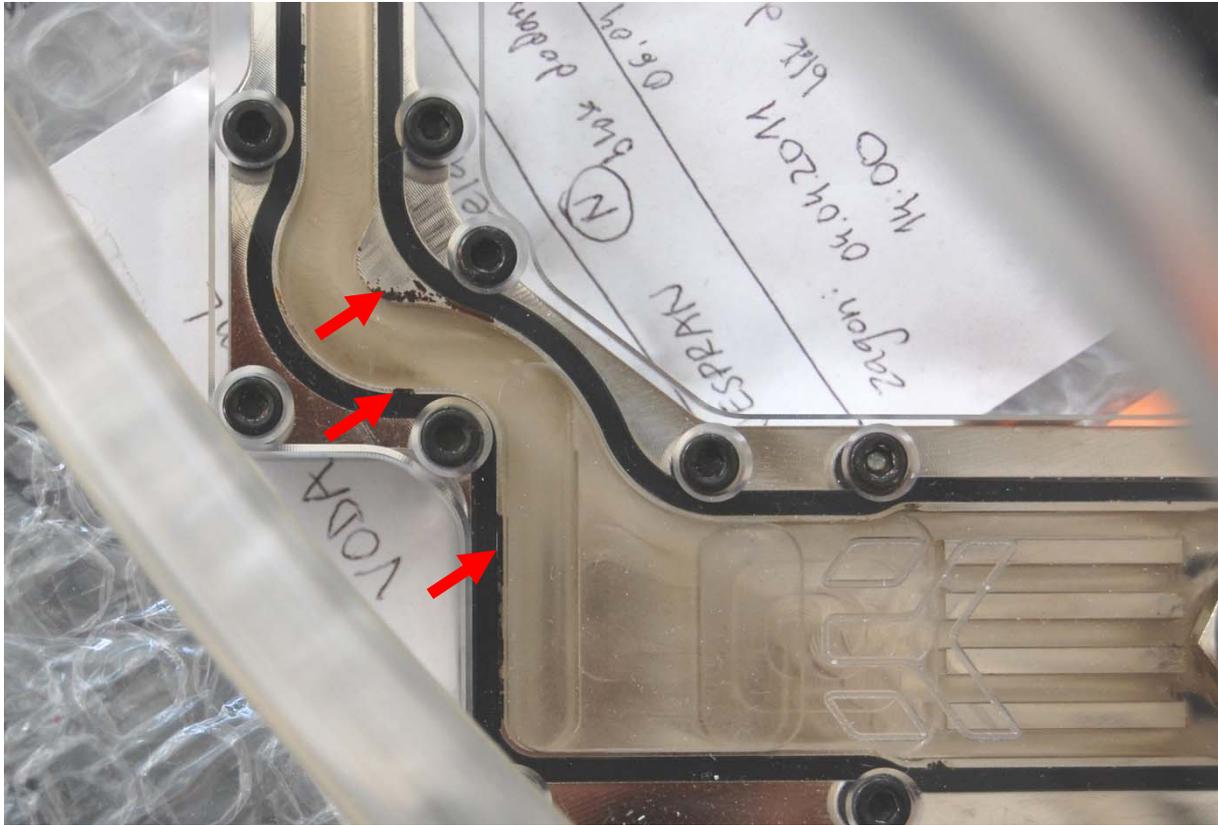






Date: May 17<sup>th</sup>

Observation: Obvious states of corrosion between the water-cooling block and plexi-glass top





Date: May 23<sup>rd</sup>

Observation: Obvious state of corrosion. Clear copper can be seen where the nickel coating is completely removed.

Image of area 1:

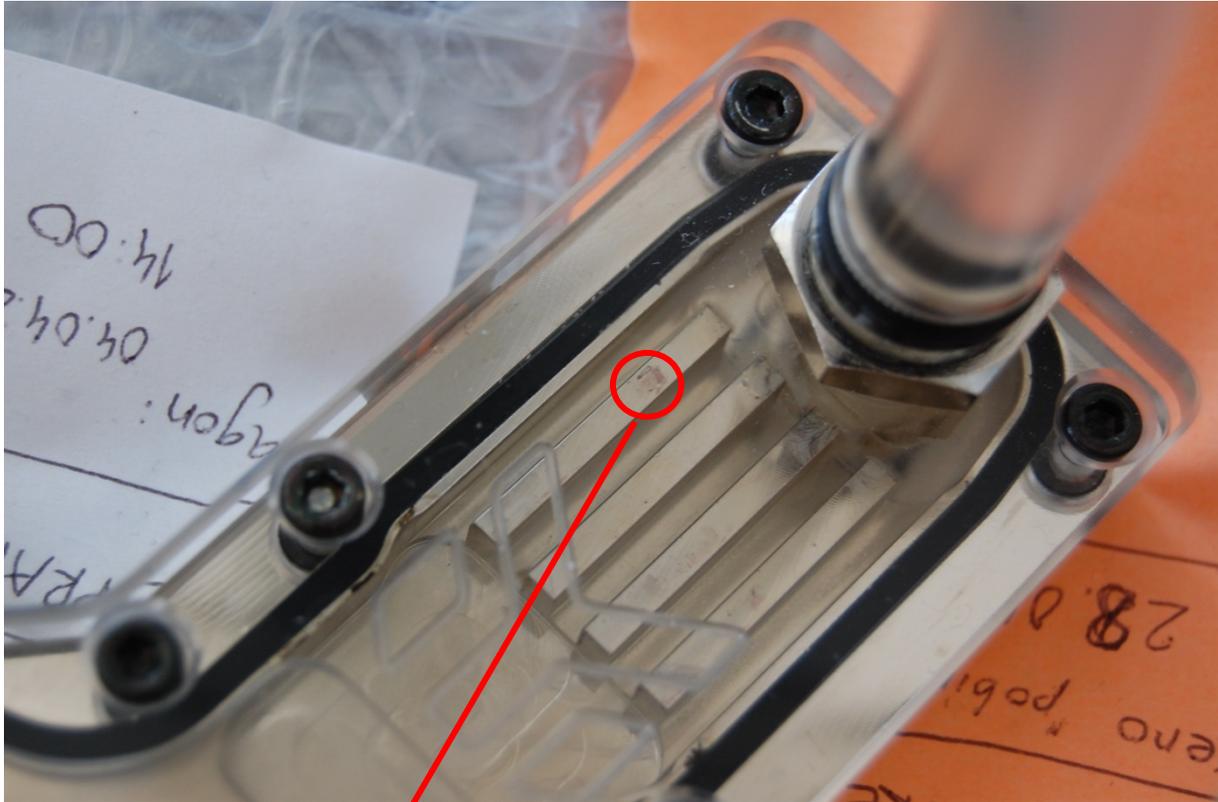
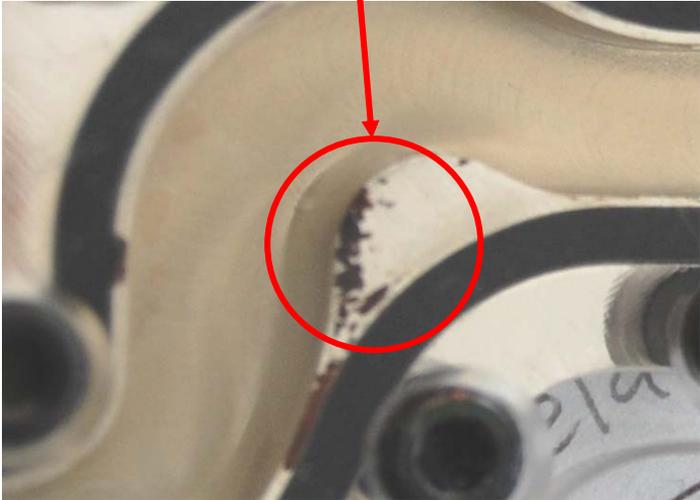




Image of area 2:

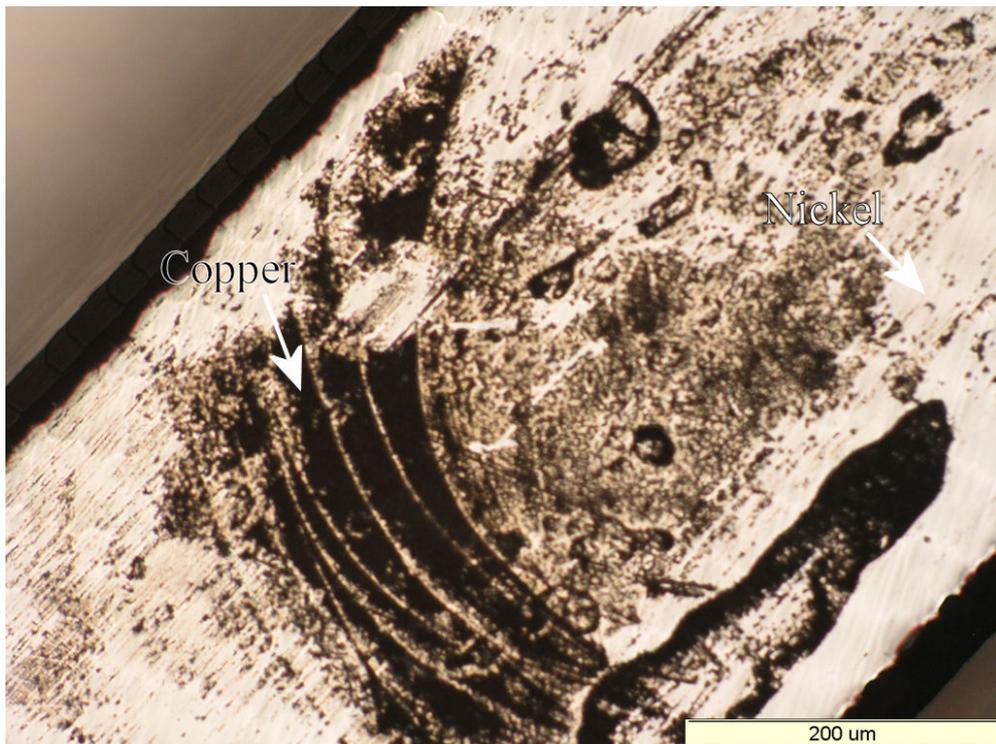


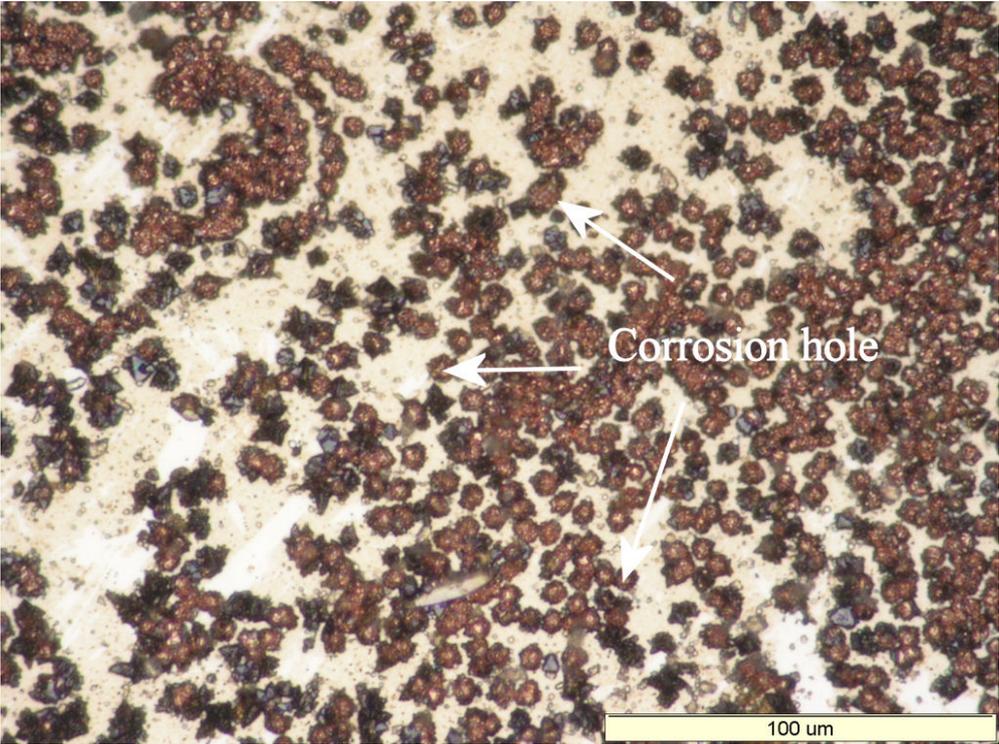
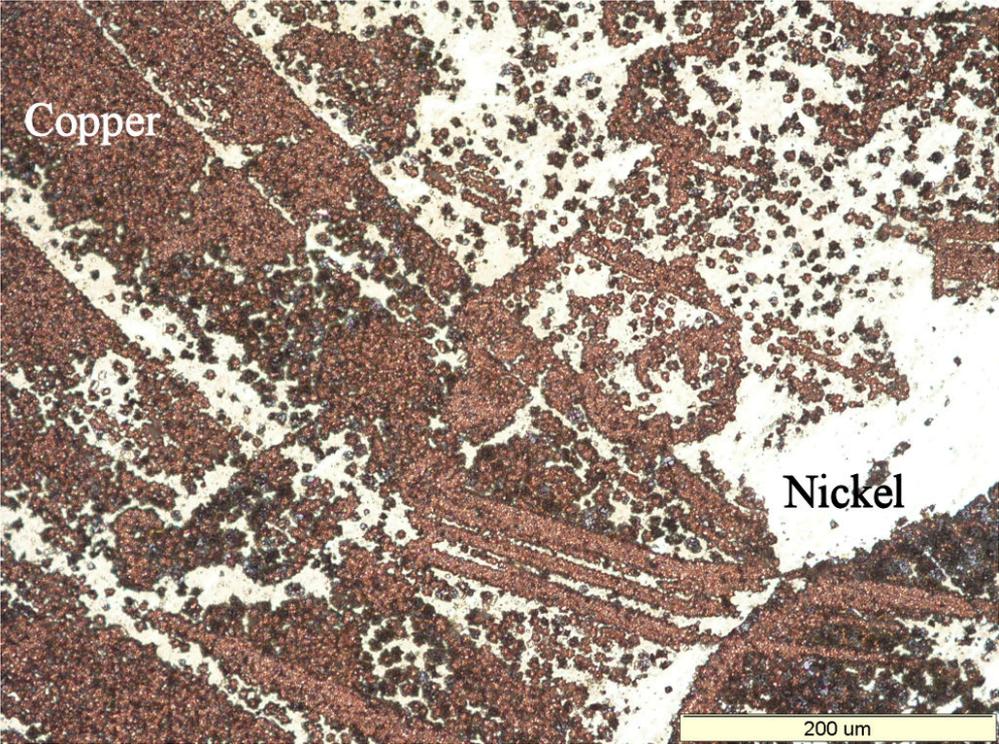


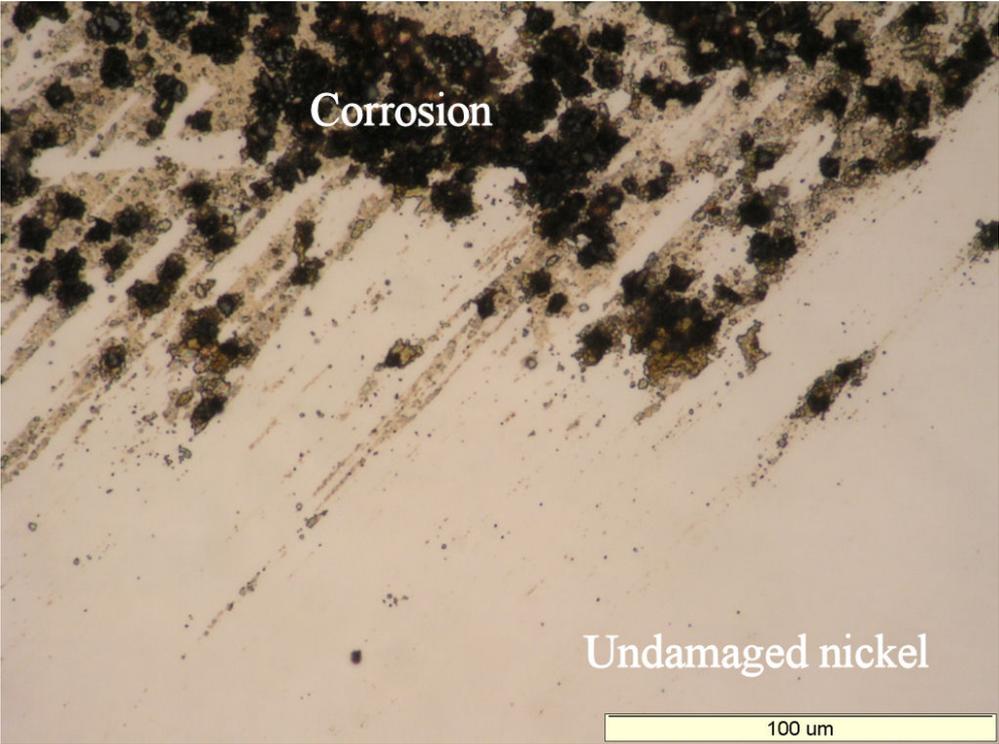
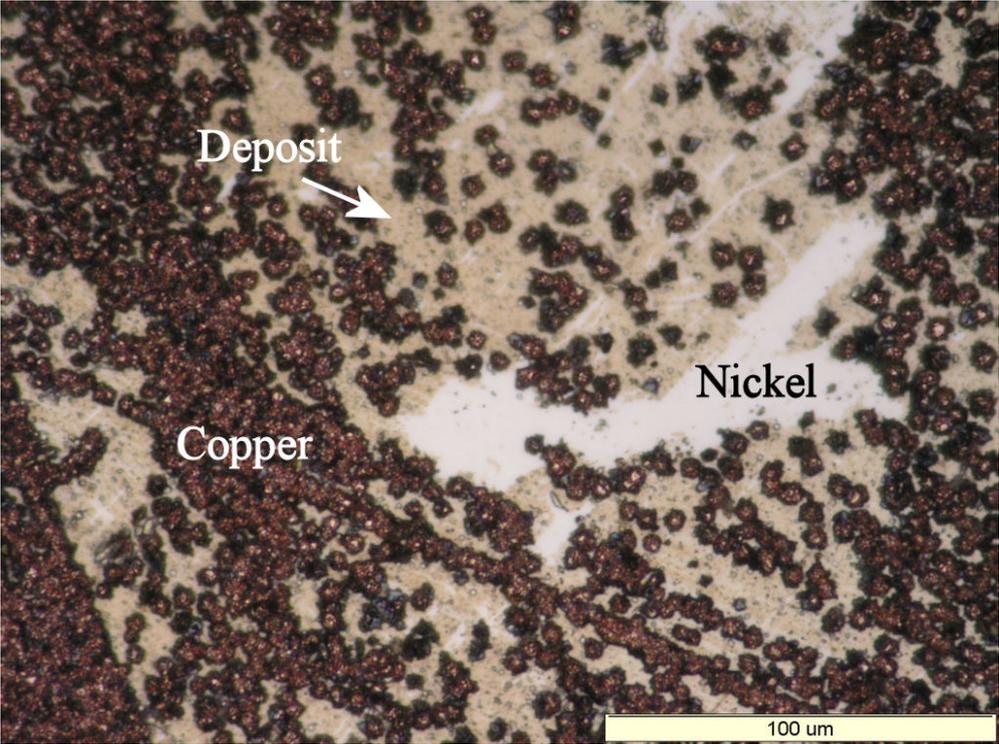
### Optical analysis of the damaged nickel-plated surface:

The nickel coating is corroded on surfaces close to the plexi-glass top of the block. The corrosion is accelerated around the areas where the copper was first exposed. Therefore, on these surfaces the nickel plating is completely removed, while on less-exposed surfaces the nickel plating is undamaged. Deposits on the nickel and copper surfaces are also visible. Deposits were also observed on undamaged nickel surfaces in the chamber of the block.

#### Area 1:

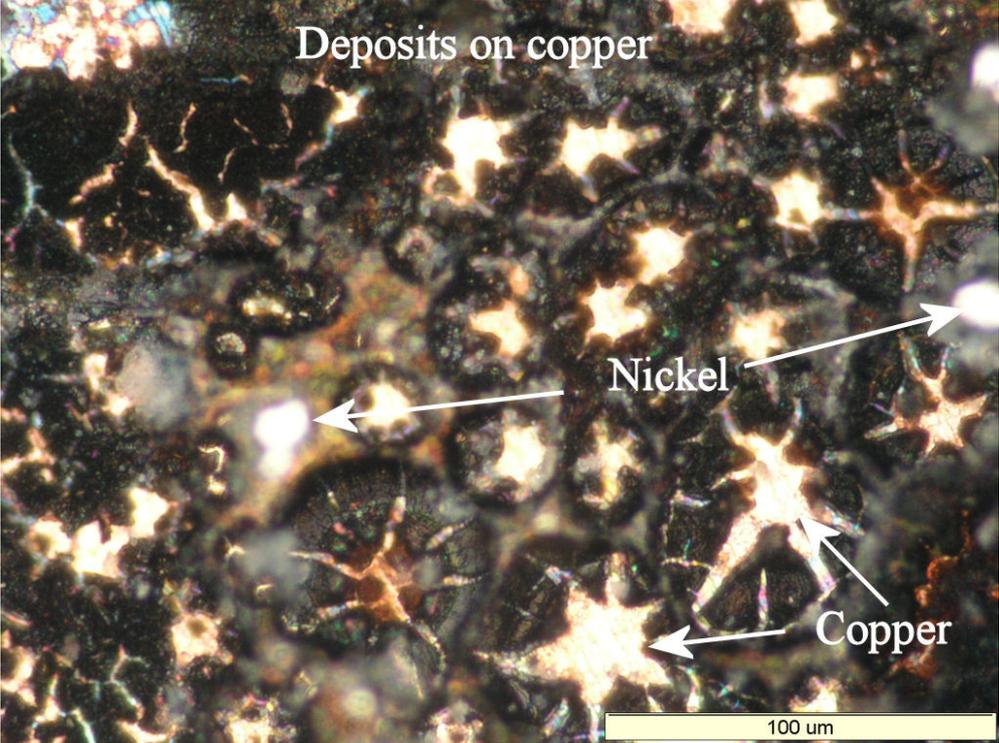
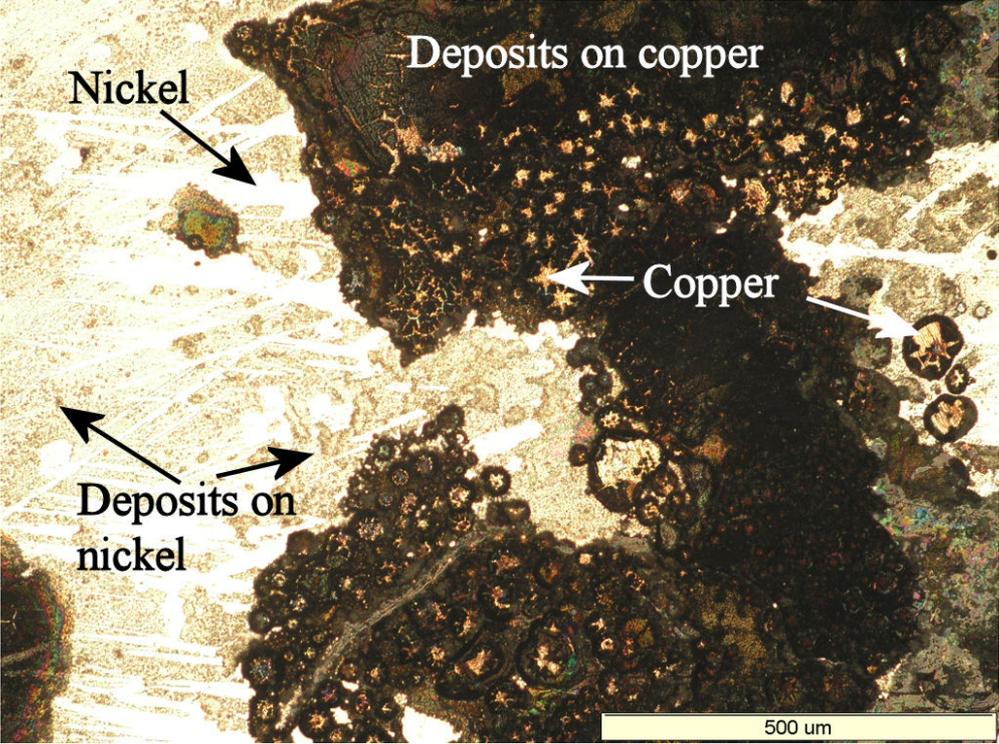








Area 2:







### Recommendation:

Corrosion can be avoided by the use of a low-conducting, anti-corrosion liquid (which, in principle, is also distilled or deionized water). It is recommended to exchange the liquid with a fresh one after a period of time to remove the possibly dissolved ions from the closed water-cooling system. The introduction of additional metals into the system (silver, etc.) or the use of ionic algacides (copper sulfate, etc.) even in minor concentrations can trigger the corrosion processes. Avoid the use of acidic substances, especially when using copper metal.

Further information on corrosion processes can be found on the internet:

[http://www.assignmenthelp.net/assignment\\_help/types-and-mechanism-of-corrosion.php](http://www.assignmenthelp.net/assignment_help/types-and-mechanism-of-corrosion.php)

<http://www.corrosion-doctors.org/pict-type.htm>

[http://docs.google.com/viewer?a=v&q=cache:ynym7SxA6QkJ:onsager.bd.psu.edu/aronne/Electrochem04.pdf+copper+nickel+galvanic+cell&hl=sl&pid=bl&srcid=ADGEEShIddtL92q\\_fQzK0vj1akusgQbkTIDevMFMI9L8p8rVsXn05zyi6lwwuukjN3hAxhHIIEM51eGvZqanacNLn\\_zLJGeOx7fTEgBIaCk3H6UKx9u\\_LeEgg4if99nRqvLlbEAh\\_Txy4&sig=AHIEtbTW1eLad-YG8fMfTqrJoQllQkTckQ&pli=1](http://docs.google.com/viewer?a=v&q=cache:ynym7SxA6QkJ:onsager.bd.psu.edu/aronne/Electrochem04.pdf+copper+nickel+galvanic+cell&hl=sl&pid=bl&srcid=ADGEEShIddtL92q_fQzK0vj1akusgQbkTIDevMFMI9L8p8rVsXn05zyi6lwwuukjN3hAxhHIIEM51eGvZqanacNLn_zLJGeOx7fTEgBIaCk3H6UKx9u_LeEgg4if99nRqvLlbEAh_Txy4&sig=AHIEtbTW1eLad-YG8fMfTqrJoQllQkTckQ&pli=1)

<http://www.scribd.com/doc/7579434/Corrosion-Basic>

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# Analysis of the irregularities on the surface of water cooling blocks

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Ljubljana, June 6, 2011