

APPLICATION OF FLUX GATE MAGNETOMETRY TO ELECTROPOLISHING

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Abstract

Flux gate magnetometry is a well-established technology for non destructive diagnostics applied to the monitoring of magnetic fields up to nanoTesla. Up to now its application to chemical and electrochemical processes remains still unexplored. The authors have applied such diagnostics to the electropolishing, evidencing a plethora of experimental evidences that can be useful both for a better understanding of the process and for a better design of electropolishing cathodic configurations. The main idea however under the detection of the magnetic signal during the electropolishing consists in the possibility of a local diagnostics of the electropolishing by contact-less probes. While the electrical polarization curve is an integral signal representative of the whole electrolytic cell, the detection of the magnetic signal gives a point by point information. Nevertheless only relative, and not absolute, measurements can be done, new chemical etching recipes can be easily created by just monitoring the reaction velocity that is proportional to the magnetic signal detected.

Advantages of flux gate magnetometry applied to Niobium chemical etching

The idea is simple, but original and in the authors' opinion of high efficacy and of wide applicability not only to the problem of cleaning superconducting cavities but to the galvanic industry in general. Without the need of any cryogenics, Flux Gate Magnetometers (FGM) can detect magnetic fields up to the nanoTesla scale. In chemical processes, several oxy-reduction reactions are involved. In standard Niobium Buffered Chemical Polishing (BCP) indeed, Nitric acid oxidizes Niobium; the hydrofluoric acid reduces the oxide into a salt that is soluble in water; Phosphoric acid complexes the surface meanwhile etching and it has mainly the role to moderate the reaction. As a consequence, during chemical etching, there is a charge transfer, to which it is obviously linked a magnetic field. In a previous work [1] we have proved that such a field is easily detectable at room temperature by means of a flux gate magnetometer. Fig. 1 displays the magnetic field spectra from 0.1 to 1.5 Hertz for 6 different Niobium BCP recipes, varying the Phosphoric acid percentage of increments of 0,2 starting from BCP 1:1:1 up to BCP 1:1:2. The signal detected in absence of acid is also reported as a reference. The detection of a full spectrum, instead of a single point at fixed frequency, is a very useful information for two reasons. First, the

acquisition over a whole frequency range of thousand and thousand points makes possible to extract the magnetic field value from noise with high accuracy. Then, the information extracted from a frequency response is twofold: we can measure the dependence versus Phosphoric acid concentration of both the magnetic field effective value and its derivative. In an equivalent circuit representation of chemical etching, indeed, the capacity of the interface between metal and acid is better explored by high frequencies, the resistivity associated instead to the diffusion of species across the liquid is better explored by low frequencies.

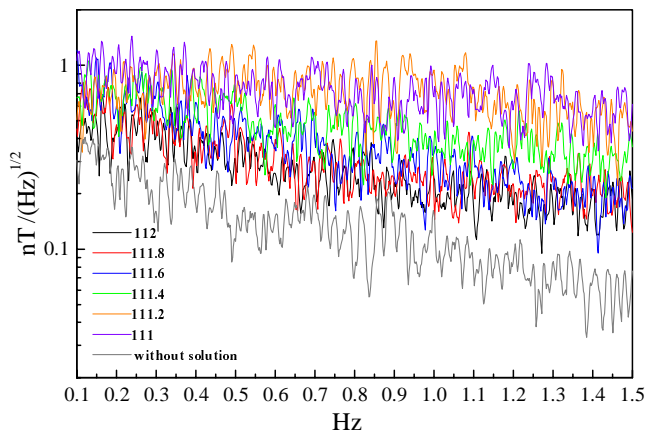


Figure 1: Spectrum of the magnetic signal versus frequencies. Passing from BCP 1:1:1 to BCP 1:1:2, by increasing the phosphoric percentage, the signal becomes monotonically less and less intense, the etching rate also decreases.

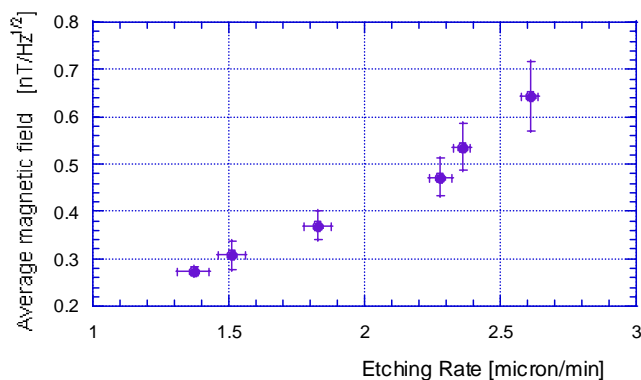


Figure 2: Average of magnetic field calculated integrating the spectra in figure 1 versus etching rate.

In fig. 2, the average magnetic field is related to the Niobium etching rate. Magnetometry therefore is a contact-less tool for measuring the relative velocity of chemical reactions. An immediate advantage can be the possibility to measure online the etching rate of a chemical reaction. Normally such a measurement is done by weighting a sample before and after the chemical attack. By means of a magnetometer outside of the bath or even encapsulated in an inert plastic tube, one can continuously add other acids or moderators inside the solution and detect the corresponding relative etching rate. Chemical etching systems made by mixing many acids and alcohols can be easily characterized in fast way changing on line the constituent percentages. New chemical etching recipes can be easily created just watching to the reaction velocity that is proportional to the detected magnetic signal.

The Fluxgate Magnetometer

The Fluxgate magnetometer is a solid state device used in several applications, such as magnetic airborne detection, search and surveillance operations, non-destructive testing of materials, This device is a directional magnetometer which working principle is based on the non-linearity of the magnetic characteristic of ferromagnetic core material in its sensing element. It measures the d.c. or the low-frequency a.c. component of the magnetic field parallel to the axis of the sensing element, with a sensitivity which ranges between 10^{-11} to 10^{-4} Tesla. In its simplest configuration the sensor consists of a cylindrical core of high permeability material around which two coaxial coils have been wound. One coil may be called the "bias coil" and the other the "sensing coil", as shown in the basic sensor configuration of Fig.3.

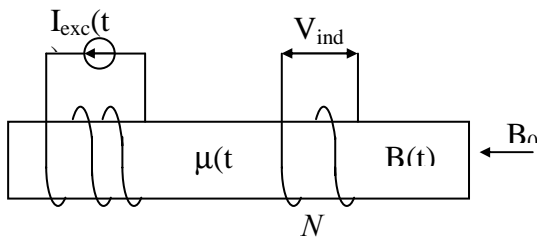


Figure 3: Bare sensor configuration. The sensor core is excited by an a.c. current I_{exc} in the excitation winding so that the core permeability $\mu(t)$ is modulated at same frequency. B_0 is the measured d.c. magnetic field and $B(t)$ the corresponding field in the sensor core. The voltage output in the pick-up coil winding with N turns is V_{ind} .

The fluxgate provides a voltage which is proportional to the applied field, the basic analytical description may start from the Faraday law:

$$V_{ind} = d\Phi/dt = d(NA\mu_0\mu(t)H(t))/dt$$

Where $\Phi=BA$ is the magnetic flux in the material and A is the area of the sensor perpendicular to the magnetic field; $H(t)$ is the magnetic field in the sensor core and $\mu(t)$ is the sensor core relative permeability. The excitation field causes the time dependence of the core permeability. In the design of a real sensor the magnetic field H , due to demagnetisation effects, is lower than the measured field H_{exc} outside the sensor core. For this reason the output equation of the induced voltage becomes:

$$V_{ind} = NAdB/dt = NA\mu_0H_{ex}(1-D)/[1+D(\mu-1)]^2 d\mu(t)/dt$$

Where D is the effective demagnetising factor.

The magnetic signal is detected generally by using a Phase Sensitive Detection (PSD), further details about the electronics characteristics of such magnetometers are discussed elsewhere [3]. The PSD technique used for the sensor enables it to work in a bandwidth ranging from d.c. to a few kHz, typically 3-5 kHz.

The noise which limits the sensitivity of a fluxgate is determinate by Berkhausen noise associated with movement of domain walls in the core as bias is applied [4]. The resolution of the fluxgate magnetometer is principally limited by the stability of the sensor zero. The change of the offset depends by the noise level and on the time instability of the sensor [5]. The spectral density of the magnetic field noise is roughly constant from frequencies below about 1Hz up to a 1kHz. In high quality commercial systems the corresponding noise level can be as low $20\text{pT/Hz}^{1/2}$ in a magnetically shielded chamber.

The fluxgate sensitivity value, compared with SQUID (Superconducting Quantum Interference Devices) magnetometer, $0.07\text{pT/Hz}^{1/2}$ measured in the same shielded conditions is clearly worse. Nevertheless the noise level of the fluxgate is so low that a successful adaptation regarding the material of the sensor, the geometry, the electronic detection and the noise rejection technique, should greatly enhance the accessibility of certain chemical corrosion studies in locations where cryogenics facilities are not available for SQUID sensors. In particular the fluxgate magnetometry might be used in low cost systems for monitoring the ongoing corrosion in metallic systems at manufactory level.

Magnetometry applied to the electropolishing of Copper

Flux gate magnetometers placed in the neighbourhood of the small electrolytic cells of fig. 4 and fig. 5 can detect without difficulty the magnetic signal associated to the electrolytic process. When a real superconducting cavity is electropolished the current density is even so high that flux gates can be easily saturated. In such a case, it is possible either to arrange the sensor more far from the cell or to use hall probes instead than flux gates.

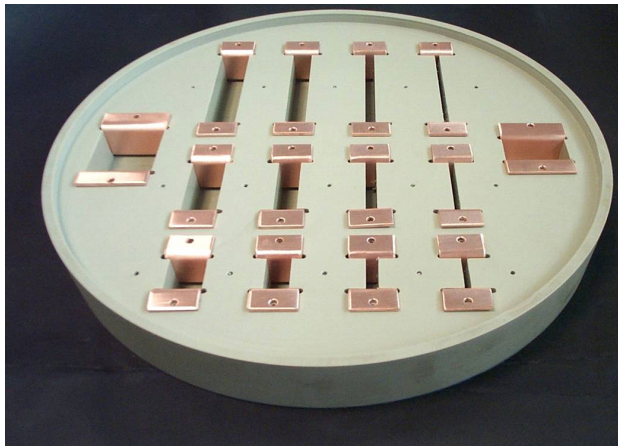


Figure 4: Rectangular electrolytic cells of different width and length for the magnetometer scanning.

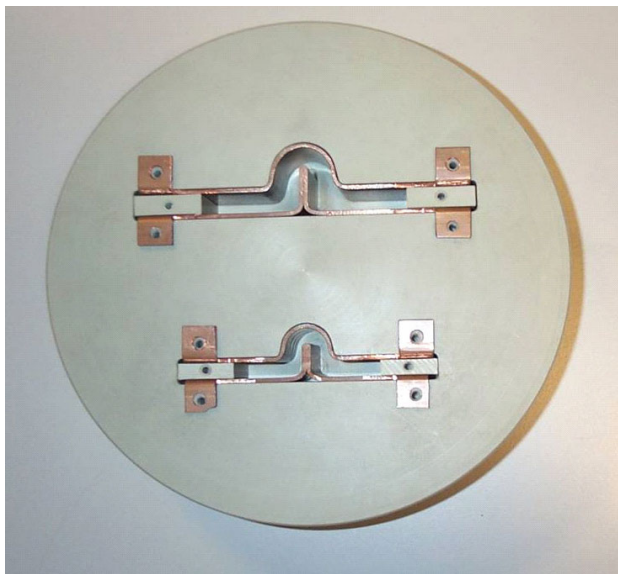


Figure 5: Cavity shaped electrolytic cells of different size. The cathode inter-changeability allows the possibility to investigate different cathode geometries, starting from that of a simple rod cylindrical cathode up to that of an equatorial disk perpendicular to a central shaft.

The main advantage of flux gate magnetometry applied to the electropolishing of a cavity is the following: instead of detecting a signal mediated all over the two electrodes, a sensor placed outside of the cavity measures just the polarization curve in the point of measurement.

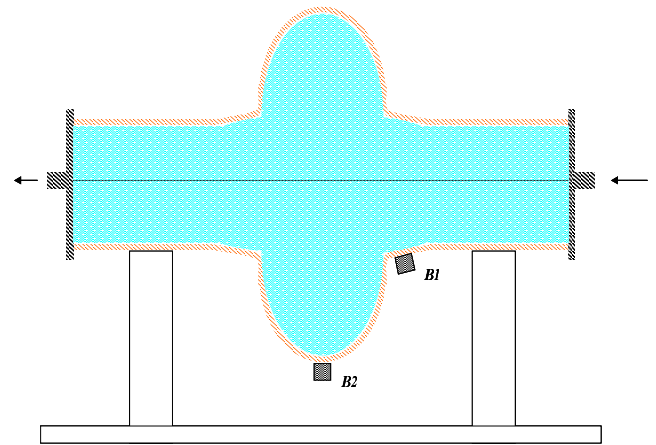


Figure 6: While the electrical signal is an integral over the whole surface of anode and cathode, the magnetic signal displays the local signal, just where the magnetometer is located.

Moreover the cathodic contribution can be separated by the anodic one. Fig. 7 reports the Magnetic polarization curve detected in the same electrolytic cell both at the cathode and at the anode side. Fig. 8 reports for comparison the relative I-V electrical characteristics

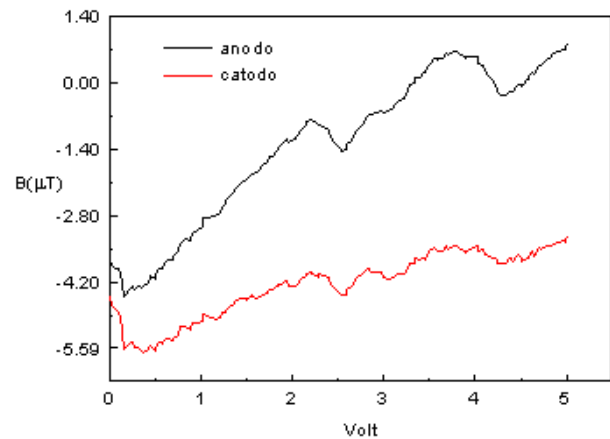


Figure 7: Magnetic signal versus voltage detected respectively at the anode and at the Cathode on an electrolytic cell.

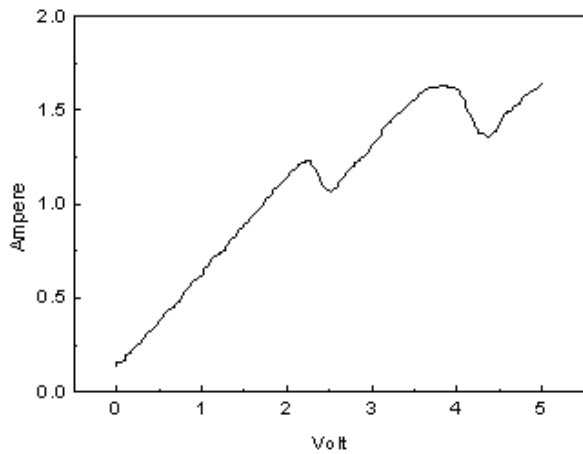


Figure 8: I-V Polarization curve for the same electropolishing cell of fig. 4.

From fig. 7, it is visible that the main electrochemical activity is mainly developed at the anode, where the copper is phosphated, rather than at the cathode, where hydrogen is developed. Moreover, if the magnetometer is moved from anode to cathode along the electrolytic cell of fig. 7, it is possible to measure the profile evolution of magnetic field along the cell axis, directly connected to the charge diffusion across the solution, as displayed in fig. 9.

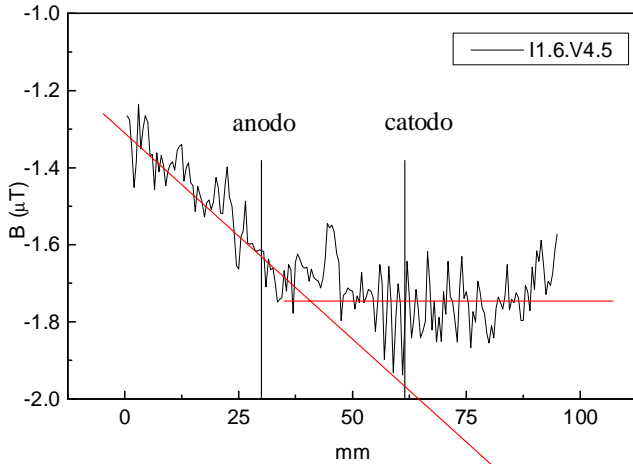


Figure 9: Magnetic field profile scanning the electrolytic cell from anode to cathode.

After a proper scaling of the units, in fig.10 it is visible a total superposition of the I-V and of the H-V characteristics. Since the control of the electrolytic polishing of metals is done by setting the voltage in the plateau, fig. 10 proves that the process can be also controlled by following the magnetic characteristics.

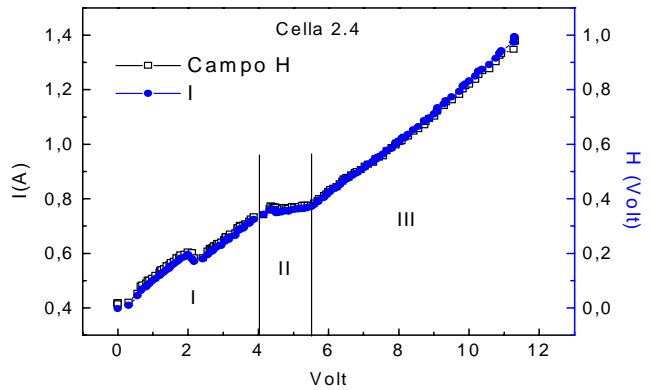


Figure 10: Magnetic and Electrical Polarization curves.

In a previous paper we have proposed a new method for controlling the electropolishing process [6]. We try to minimize parasitic problems as material pickling or gas evolution, by searching the best working point of the I-V characteristic and by following it during the whole process. The method consists in computer monitoring the I-V characteristic. The process is driven in voltage. An automatic program displays the numeric derivative of I versus V. The working point is chosen as the minimum of the dI/dV derivative, i.e. the minimum of bath differential conductance that corresponds to the point of maximum resistance of the viscous layer. This technique automatically finds the best polishing conditions, without caring of the bath composition and of electropolishing parameters. In fig. 11 it is displayed the standard I-V characteristics and the analogical derivative of the magnetic field detected by a flux-gate magnetometer at the center of the cell. It can be easily seen that the minimum of the magnetic characteristics is located just at the same voltage value where the current reaches a plateau. The computer feedback circuit used for electropolishing, instead than controlling the I-V characteristics can easily control the derivative of the magnetic signal. The advantage is that the flux gate can be moved on the surface finding for each point the best value of the electropolishing voltage. In such a way for complex parts to electropolish, the best cathode can be optimized by the analysis of local H-V characteristics.

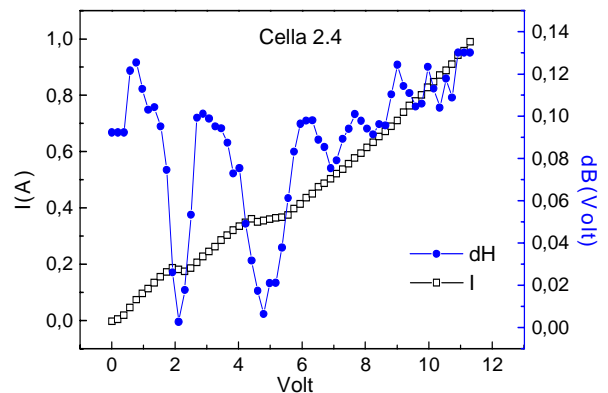


Figure 11: The minimum of local magnetic field derivative corresponds to the high resistivity of the anodic.

double layer. By locking such a minimum, one automatically finds the best polishing conditions.

Magnetic tomography of electrolytic cells

If the electrolytic cell is scan by the flux gate magnetometry, it is possible to get a tomography of the electrolytic process at different voltages. In particular the ion diffusive process can be easily monitored and it can be put in relation with the shape of the Polarization curve. It is possible to acquire simultaneously the three magnetic field components with three perpendicular sensors at once, or even to superpose the three field components measured one by one by the same sensor.

We have measured the magnetic field map of a 40mm x 50 mm electropolishing cell scanning from anode to cathode by flux gates in gradiometric configuration. We have defined the z-axis perpendicular to the cell plane, and the x-axis parallel to the normal to the electrodes. In fig. 12 it is reported the plot of the z-component of the magnetic field at different potentials respectively 1.5V, 4.5V and 6.5V.

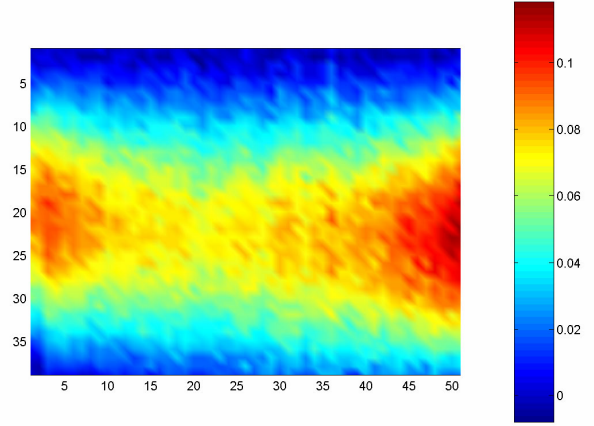


Figure 12: Y- component of the magnetic field detected in a plane parallel to the cell. Field units are in TESLA, Currents are in A/m-2.

The deconvoluted and inverted magnetic maps give rise to a kind of current distribution tomography for the electrolytic cell at various potentials. Inverting the Biot-Savart law

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int \frac{\mathbf{J}(\mathbf{r}') \wedge (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d^3r',$$

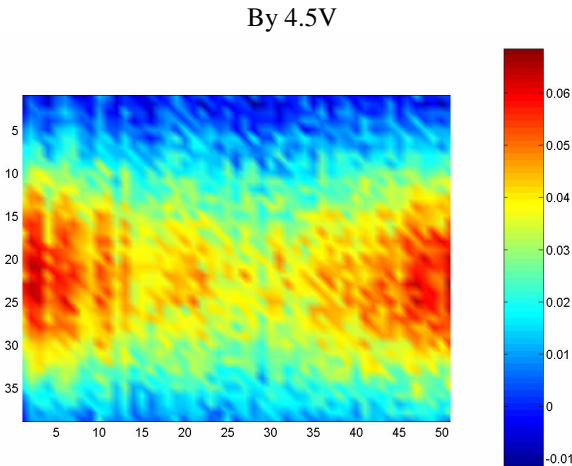
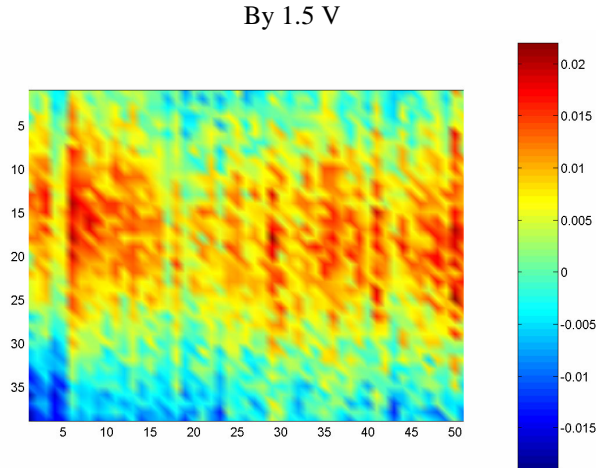
assuming the continuity equation and the condition $J_z = 0$, it is possible to deduce the current density induced by the magnetic field [7].

$$\begin{aligned} \mu_0 \mathbf{H}_{ind} \cdot \hat{\mathbf{i}} &= \mu_0 H_x(x, y, z) = \\ &= \frac{\mu_0}{4\pi} \iiint \frac{J_y(x', y', z') \cdot (z - z') - J_z(x', y', z') \cdot (y - y')}{\sqrt{[(x - x')^2 + (y - y')^2 + (z - z')^2]^3}} dx' dy' dz' \end{aligned}$$

$$\begin{aligned} \mu_0 \mathbf{H}_{ind} \cdot \hat{\mathbf{j}} &= \mu_0 H_y(x, y, z) = \\ &= \frac{\mu_0}{4\pi} \iiint \frac{J_z(x', y', z') \cdot (x - x') - J_x(x', y', z') \cdot (z - z')}{\sqrt{[(x - x')^2 + (y - y')^2 + (z - z')^2]^3}} dx' dy' dz' \end{aligned}$$

$$\begin{aligned} \mu_0 \mathbf{H}_{ind} \cdot \hat{\mathbf{k}} &= \mu_0 H_z(x, y, z) = \\ &= \frac{\mu_0}{4\pi} \iiint \frac{J_x(x', y', z') \cdot (y - y') - J_y(x', y', z') \cdot (x - x')}{\sqrt{[(x - x')^2 + (y - y')^2 + (z - z')^2]^3}} dx' dy' dz' \end{aligned}$$

The current is obviously mediated all over the cell thickness. The analysis of the single deconvolution components can provide the bidimensional distribution of the current density. In fig. 13, there are displayed the map of the current density x-component map deconvoluted by the maps of the magnetic field y-component deconvoluted by the maps of the magnetic field z-component in fig. 12.



By 6.5 V

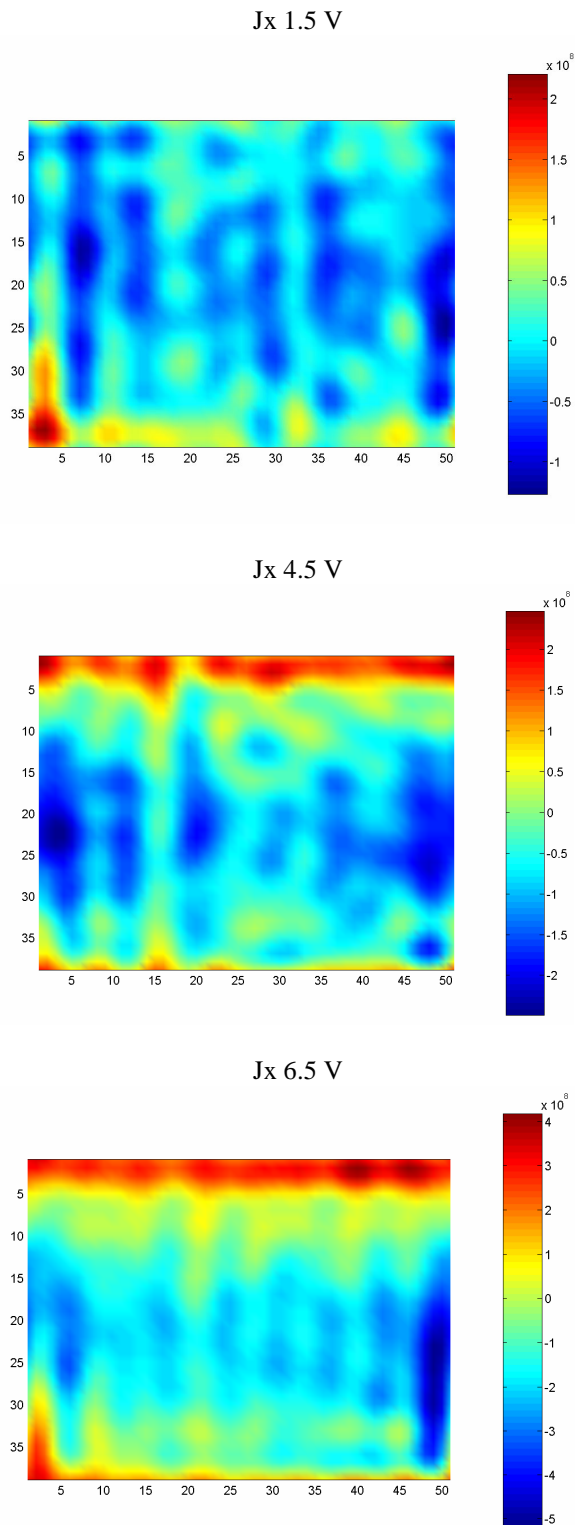


Figure 13: Maps of the current density deconvoluted from the magnetic field at different voltages, respectively 1.5V, 4.5V and 6.5V.

We can notice that in the Fourier space, it is possible to exactly invert the third equation [8], by means of a third equation correlating the two planar components of current density. If we choose the continuity equation

$(\nabla \cdot \mathbf{J}(\mathbf{r}) = 0)$, then we must hypothesize that $J_z = 0$ and that the current flows into a loop limited inside the measurement plane, i.e. the acquisition must contain also the area external to the source for an extension at least equal to the same loop surface. Of course any noise, dishomogeneity, spurious gradients and so on will be found non locally in the current distribution.

Conclusions

Flux Gate Magnetometry is a very powerful methodics for investigations of both chemistry and electrochemistry: by means of such technique indeed some of the authors [2] have easily succeeded in creating hundreds of new recipes either for the chemical etching and for the electropolishing of several materials that normally are considered “difficult to clean” by the galvanic industry. Besides superconducting cavities, indeed some of the considerations reported in this paper have been useful for solving several problems of direct industrial applicability such as: the electropolishing of gold without cyanides, the electropolishing of magnesium, aluminium and alloys for spectacles; the cleaning of titanium for dental implantology, prothesis and cardiac valves, the electropolishing of stainless steel and cast iron for general mechanical applications, and of other alloys for electronic applications.

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