



# TRIBOCHEMISTRY VERSUS NANO-TRIBOLOGY I.

## THEORETICAL CONSIDERATIONS ON MAKING A TANDEM NANOSCOPE

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Previous tribochemical studies showed that the high activation energy of reactions between solids covered by mechanical energy has not exclusively be thermally originated as that had been adopted formerly. For studying of tribochemical elemental effects, some theoretical considerations of combination atomic force microscope (AFM) and scanning tunneling microscope (STM) techniques using one dual tip cantilever have been discussed to develop a solid base to make experimental setup called *Tandem Nanoscope*.

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### Mechanical activation of chemical reactions

The general course of mechanically activated chemical reactions, observed in many experiments, for instance in a ball mill, can be described by following principal diagram:

### Introduction

Tribochemistry is a branch of chemistry dealing with the chemical and physico-chemical changes of solids due to the influence of mechanical energy.<sup>1-12</sup> Nano-tribology is a branch of tribology dealing with friction and wear processes in nanometer scale using scanning probe microscopy (SPM) methods.

The most fascinating discovery of tribochemical studies performed worldwide in the last decades was that the high activation energy of reactions occurring between solids and covered by mechanical energy do not exclusively originate from thermal sources as that had been adopted formerly. In order to study the elements of these tribochemical effects, some theoretical considerations of combination atomic force microscope (AFM) and scanning tunneling microscope (STM) techniques using one dual tip cantilever have been discussed in order to develop a solid base to make experimental setup called *Tandem NanoScope*. The article here present these theoretical considerations and conclusions about making possibility of a *Tandem nanoscope*.

### Tribochemistry

#### Definitions

Tribochemical synthesis, sometimes called mechanosynthesis including the current state of the art, as well as opportunities and challenges to it becoming a mainstream synthetic technique. It nowadays covers industrial aspects, inorganic materials, cocrystals, pharmaceutical applications, organic synthesis, discrete metal complexes, extended metal-organic materials<sup>13</sup> (MOFs) and has very close connections to nanotechnologies

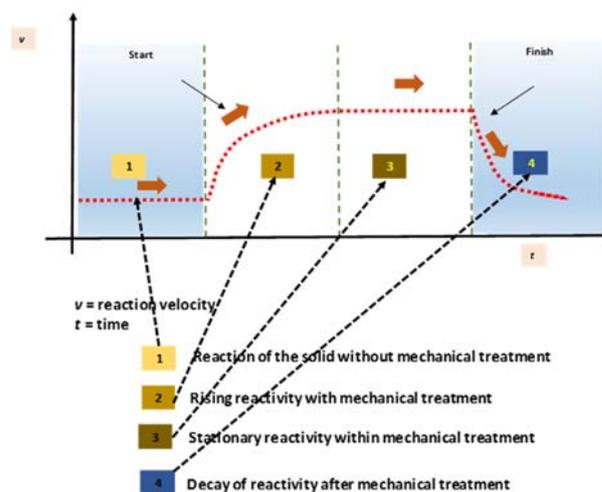
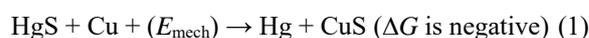


Figure 1. The course of tribochemical reactions<sup>3</sup>

At the beginning there is the low, only thermally activated reactivity, followed by the rising activity with mechanical treatment arriving to a stationary high level. Subsequent to the mechanical treatment there is decay of the reaction velocity and after treatment remains the state of the so called mechanically activated solid at some higher level.

There are tribochemical reactions with positive affinity, which are thermally activated reactions, as for instance HgS (Cinnabar) decomposition by trituration in a Cu mortar by a Cu pestle with a little amount of acetic acid producing elemental mercury [ancient Greece 400 BC].



There are also tribochemical reactions with negative affinity, that are non-thermally activated reactions, such as milling of rocksalt (NaCl) in presence of Hg produces elemental sodium (as amalgam) and chlorine.<sup>12</sup>



One can see that for a set of tribochemical reactions in “*statu deformandi*” (in time of mechanical activation) it can be said that characteristically they are proceeding whilst producing non-equilibrium negative affinities (Table 1).

**Table 1.** Some Tribochemical reactions with negative affinity (positive free enthalpy)<sup>7</sup>

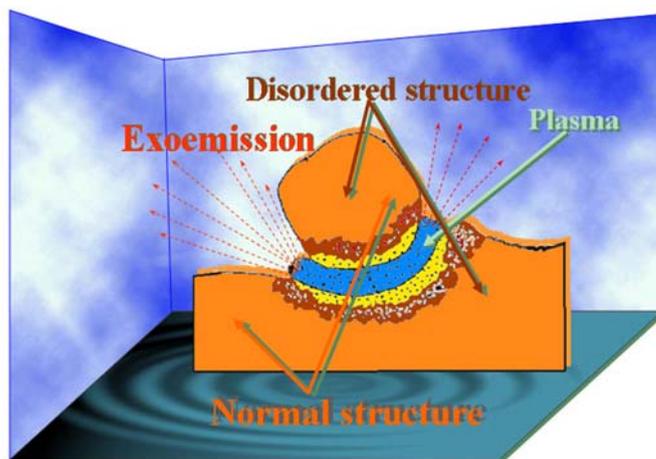
No.	Reaction	$A_{298\text{K}} \text{ kJ mol}^{-1}$
1	$\text{BaO}_2 \rightarrow \text{BaO} + \frac{1}{2} \text{O}_2$	-55.2
2	$\text{SiC} + 2\text{H}_2 \rightarrow \text{Si} + \text{CH}_4$	-58.9
3	$\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2$	-62.4
4	$2\text{Cu} + \text{CO}_2 \rightarrow 2\text{CuO} + \text{C}$	-140.2
5	$\text{Au} + \frac{3}{4} \text{CO}_2 \rightarrow \frac{1}{2} \text{Au}_2\text{O}_3 + \frac{3}{4} \text{C}$	-311.5
6	$\text{Fe}_3\text{O}_4 + 2\text{C} \rightarrow 2\text{CO}_2 + 3\text{Fe}$	-330.2
7	$2\text{MgO} + \text{C} \rightarrow \text{CO}_2 + \text{Mg}$	-744.9

In the mechanically induced electrochemical deposition of metals without external current, contrary to the electromotive series, the “Tribogalvanic Effect” has a minimal affinity of  $-300 \text{ kJ mol}^{-1}$ .<sup>14</sup> It has been shown that the negative affinity of tribochemical reactions does not decrease with rising temperature, as it might be expected, but increases instead (Table 2).

**Table 2.** Temperature dependence of the *negative* affinity for two tribochemical oxidation reactions of copper calculated by the 1<sup>st</sup> UHLICH approximation

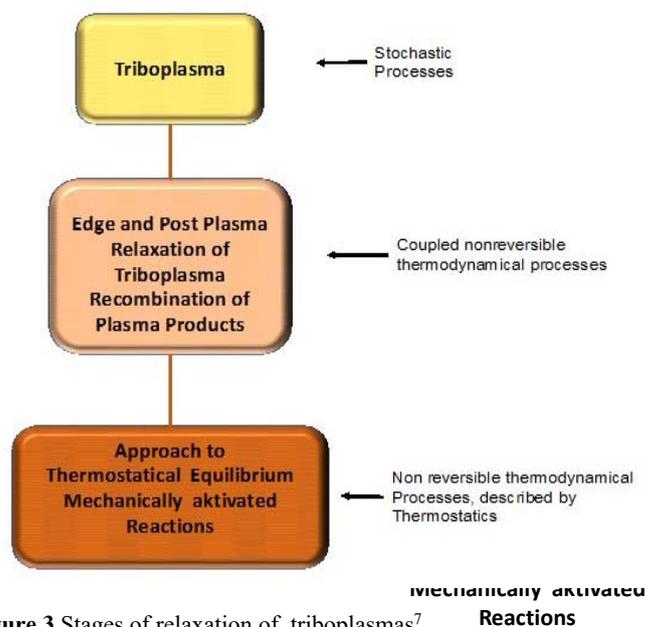
Temperature	Basic Affinity, $A^0_{\tau} \text{ kJ. mol}^{-1}$		
	298K	1000K	2000K
$4\text{Cu} + \text{CO}_2 \rightarrow 2\text{Cu}_2\text{O} + \text{C}$	101.7	199.6	342.3
$2\text{Cu} + \text{CO}_2 \rightarrow 2\text{CuO} + \text{C}$	138.9	271.1	466.1

The experimental results suggest that a common thermal activation can be excluded with high probability. Following the principle of least contradictions the hypothesis of the “Magma-Plasma-Model” was developed.<sup>3</sup> The “Magma-Plasma-Model” proposes that local temperatures greater than  $10^4 \text{ K}$  in ultra-short-time can be generated at mechanical impact points, associated with transient (tribo-) plasmas and the ejection of energetic species including free electrons.<sup>14</sup>



**Figure 2.** Magma Plasma Model (MPM) „Triboplasmas“

The energetic relaxation of triboplasmas was described by the following stages.



**Figure 3.** Stages of relaxation of triboplasmas<sup>7</sup>

### Scanning Probe Microscopy (SPM) for Nano-Tribochemistry

There are many universal scanning probe microscopes combining the use of AFM or STM.<sup>13</sup> Precisely such types of nano-analytical devices appear to be useful for the examination of elemental effects of tribochemical reactions. For this purpose a device must be designed, which can generate a tribochemical reaction “just in time” and observe directly possible magma plasmas or their relaxation processes respectively.

The idea is to use simultaneously an atomic force microscope (AFM) for the nano-tribological impacting of a metallic surface and a scanning tunnelling microscope (STM) for the examination of tribochemical reactions with atomic scale resolution.

## Tandem Nanoscope

How should such a dual function device be designed? There must be a dual tip cantilever, where one tip will function as AFM that is touching the metallic surface and generating the tribochemical action under the required circumstances. This tip must be electrically insulating. The other tip, being electrically conductive, does not touch the surface to be examined. It serves as STM analyzing the physical and chemical conversions with atomic resolution.

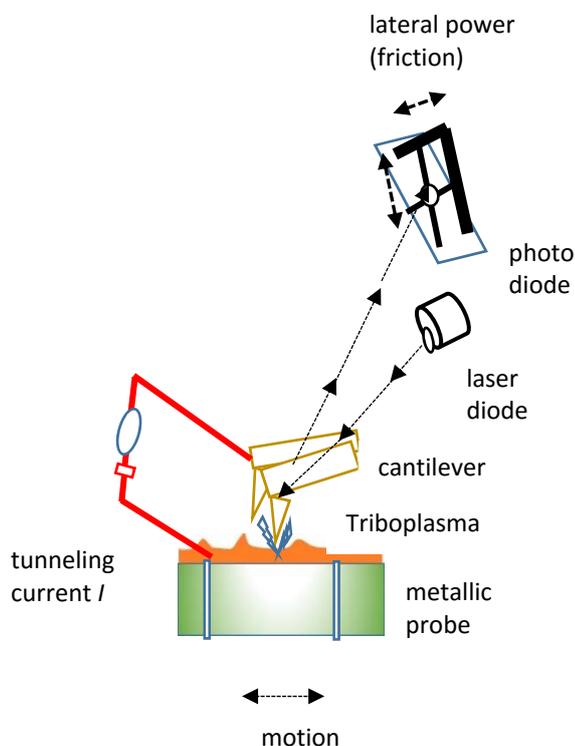


Figure 3. Tandem Nanoscope.

The device called by us “**Tandem NanoScope**”. A functional sketch with a dual tip cantilever is follows:



Figure 4. „Hammerhead“ cantilever - NIST

The dual tip device may look as shown below using an idea from the National Institute of Standards NIST, a so called “Hammerhead”. One tip serves as AFM, touching the sample surface, the other tip, coated with gold and moving in some nanometer distance to the surface will be the “watching” STM.

## Discussion

The principle of “Tandem Nanoscope” opens new perspectives to scanning probe microscopes with novel abilities for direct watching of tribochemical reactions, maybe also triboplasmas, with atomic resolutions and opens a way before building it experimentally.

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