

## 5 Spirals on Amorphous Pt

The presence of an excitable or oscillatory *medium* (in the nonlinear theory meaning the *system*) represents a requisite for the formation of spirals [1]. In both cases the states are characterized by the presence of at least two independent variables. The CO and O coverages on a Pt surface are not independent, but mutually adiabatic-dependent, in the sense that when one is set, the other rapidly converges to a given value. In the case of spiral formation on the Pt (110) single crystal, the role of the second, independent, variable is considered to be played by the surface structure. As described in section 1.4, the two states are the reconstructed (1x2), characteristic of the clean surface at room temperature and the deconstructed (1x1) for CO coverages higher than 0.2 ML. That means that although a dependence between the two variables does actually exist, it is not adiabatic, since the reconstruction slowly follows the CO-coverage.

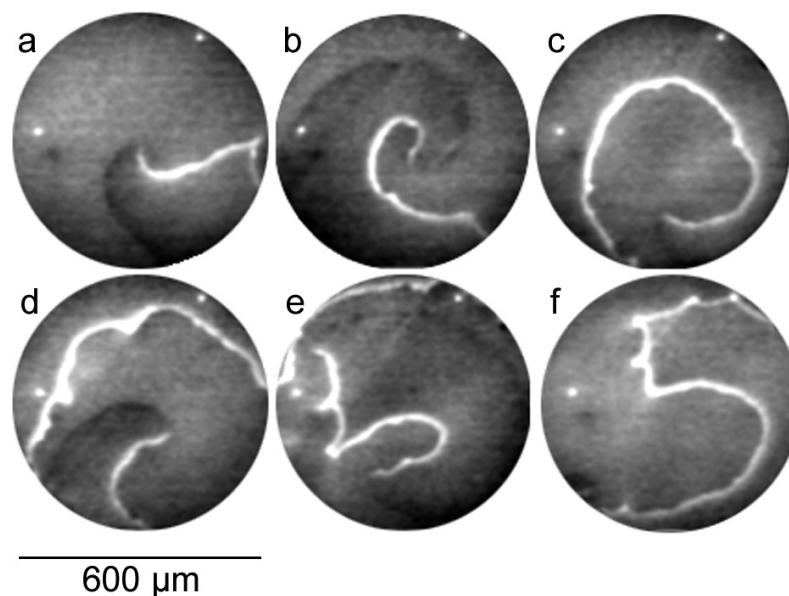


Fig 5.1 PEEM images of a spiral wave on Pt(100);  $T = 458 \text{ K}$ ,  $\Delta t = 2 \text{ s}$   $p(\text{CO}) = 2.9 \cdot 10^{-5} \text{ mbar}$ ,  $p(\text{O}_2) = 4 \cdot 10^{-4} \text{ mbar}$ .

No spirals are therefore expected on surfaces not exhibiting surface rearrangements, like Pt(111). Even on Pt(100) no fully developed spirals were found. Only rotating waves, shown in Fig. 5.1, were observed by Lauterbach and Rotermund [2]. The authors explained this behavior with the dramatic difference in propagation speed between oxygen and CO fronts.

It has been therefore quite surprising to find spiral wave formation in the CO + O<sub>2</sub> reaction on amorphous Pt. This platinum film, deposited by electron beam bombardment on a piezo material, did not show any mesoscopic grain boundaries, in contrast to polycrystalline samples, which consist of contiguous micro-crystals.

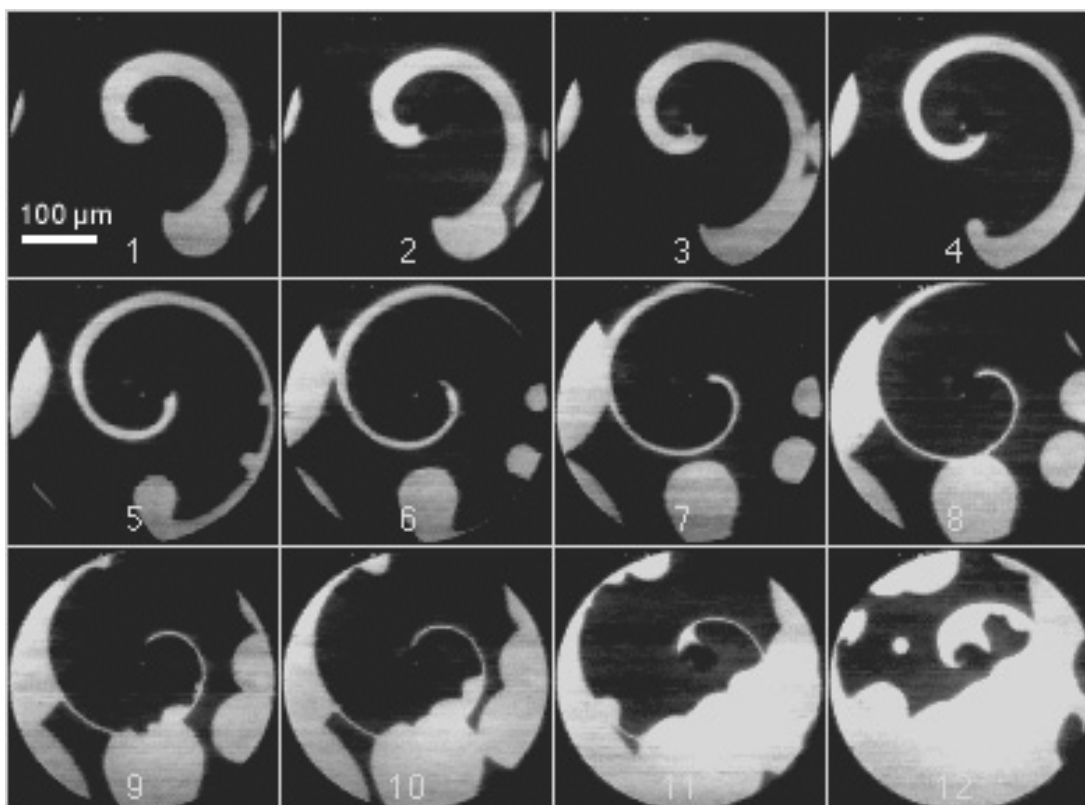


Fig. 5.2 PEEM images of a CO spiral on an amorphous Pt substrate;  $\Delta t = 5$  s;  $T = 500$  K,  $p(\text{O}_2) = 2 \cdot 10^{-4}$  mbar,  $p(\text{CO}) = 1 \cdot 10^{-5}$  mbar. In the center a macroscopic defect is visible.

Fig. 5.2 shows the time evolution of a “CO” spiral attached to a large defect. The spiral wave, although getting thinner, seems to be stable, and it is eventually destroyed by incoming CO fronts. The question whether these spiral patterns have to be considered as just mere “transients” is open. Moreover, it is not clear which phenomenon could be invoked to play the role of the *second variable*.

Possible alternative mechanisms that could lead to self-sustained oscillations, namely oxide formation [3], surface carbon deactivation [4], [5], surface roughening [6], and subsurface oxygen formation [7], [8], are in the following presented and discussed.

Sales, Turner and Maple [3] proposed that the oscillations result from periodic oxidation and reduction of the catalyst surface. The oxide shall decrease the catalytic activity by blocking adsorption sites for CO and O<sub>2</sub>. Other authors have questioned this hypothesis, since it is based on atmospheric pressure observations, for which a significant presence of contaminants could not be avoided. And indeed Yeates and colleagues [9] found large amounts of Si on the surface of single crystals that exhibited oscillations at atmospheric pressure. Moreover, no in-situ experiment has brought direct evidence for oscillations in the oxide concentrations.

Burrows and coworkers [4] on the contrary suggested that the activation/deactivation cycles are due to the presence of carbon on the surface of the catalyst, which prevents the CO adsorption. They added that this carbon species could be removed by oxygen at temperatures relevant to the oscillatory CO oxidation.

Bassett and Imbihl [7] proposed that during the CO oxidation on Pd(110) chemisorbed oxygen can be reversibly converted into a subsurface species. The subsurface oxygen is thought to lower the catalytic activity by drastically decreasing the oxygen sticking coefficient.

The latter three models do not incorporate any CO-induced surface reconstruction, and could therefore account in principle for the spatio-temporal oscillations observed (Fig. 5.6) on the CO+O<sub>2</sub>/ amorphous Pt system. For the Pt(110) surface there is, however, experimental evidence that the reconstruction plays an essential role in the oscillatory regime of the CO oxidation, as explained in section 1.5. The corresponding model, developed by Krischer et al. [10] and Bär et al. [11], has been extended by Oertzen et al.[8] to include the formation of subsurface oxygen. This *reconstruction* model, however, does not allow oscillations for the system under consideration. By neglecting surface phase transitions, no negative feedback mechanism is left, since the presence of subsurface oxygen favors an increase of the chemisorbed species, and vice versa.

As a conclusion, at present it is not possible to explain unambiguously the observed spiral formation in the CO oxidation on an amorphous Pt surface. The synergetic interaction of experimental and modeling work, however, is likely to yield in the next future progresses towards the understanding of these intriguing processes.

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