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Progress Towards More Realistic In-Situ Microscopy Observations

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As progress indicators in electron microscopy, advances in spatial resolution and in spectroscopy probably attract most frequent attention. Improved user-friendliness has also been significant even when judged in comparison with scanned probe microscopy. Evidence for developments in in-situ microscopy at least equally impressive can be found by comparing the relevant sections of the book by Hirsch et al. [1] and a more recent compilation [2].

Peter Hirsch's research group swiftly discovered the power and frustrations of in-situ microscopy. The cine film of dislocation motion observed in the earliest diffraction contrast studies [3,4], and attributed to the thermal stresses generated by the electron beam, was extremely effective in convincing the wider community that it was indeed dislocations that were being observed. In a remarkably successful in-situ hot stage experiment applied to a simple problem, the shrinkage of dislocation loops due to migration of vacancies to the foil surfaces was followed and fitted in detail to a quantitative model [5]. Any consequent feelings of euphoria were probably moderated when, in trying to employ the same equipment more ambitiously to study alloy phase transitions, the dominating effect of diffusion and reactions at the foil surfaces was observed [6]. Another hot stage project that was tackled with mixed success was to follow the recrystallisation process of grain boundary motion in heavily worked silver foils [7]. Successful cine photography was defeated by the tendency for recrystallisation to take place abruptly outside the field of view. Observations of dislocation motion under more controlled conditions of plastic deformation as well as in fracture have continued but the focus below is on surface science and catalysis work.

Despite the poor vacuum conditions, the power of TEM in studies of metal epitaxy was apparent [8] and encouraged Hirsch and Pashley to enlist the expertise of Ugo Valdre in the construction of a separately pumped UHV stage unit [9]. This system was used for several years in studies of both island and psuedomorphic growth as well as in metal oxidation [10] where much of the work has been confirmed in more modern equipment [11] capable of revealing the surface reconstructions associated with the oxide nuclei. For clean surface studies, these TEM methods are increasingly challenged by other techniques, including reflection electron microscopy (which first revealed the nucleation of surface reconstructions at surface steps [12]), photoemission electron microscopy (PEEM)[13] and, most particularly, scanned probe microscopy (SPM), whose popularity with the wider surface science community vividly illustrates the importance of user-friendliness. These other approaches have been compared [14] and offer varying levels of spatial resolution, nanoanalysis and imaging speed. They generally employ bulk sample surfaces rather than thin film surfaces with advantages for specimen preparation and surface cleaning but, in some cases, with disadvantages for ionisation damage and beam charging.

The drive towards in-situ microscopy of catalytic processes received early stimulation from some spectacular TEM observations [15] but places extreme demands if realistic pressures and temperatures are to be achieved. Peter Hirsch's long lasting influence here can be traced to the Oxford project for high voltage in-situ microscopy[16]. In some sense this is the ancestor of the

much more ambitious medium voltage, high resolution, environmental TEM equipment designed and developed by E. Boyes and P.L. Gai [17] after their move from Oxford to Dupont and used with remarkable success in many catalyst investigations [2,18]. A later version of this equipment installed at Haldor Topsoe A/S recently yielded intriguing results on the distribution of Ba promoter in Ru ammonia synthesis catalysts [19].

Environmental SEM and PEEM both offer some competition to TEM methods for work under gas pressure but cannot compete in terms of spatial resolution. The most serious potential competitor here is undoubtedly SPM but for some reason the challenge has been slow to develop. Recent STM work in the few bar range [20,21] could surely be extended to higher pressures or even liquid operation conditions on catalysts (provided any oxide support is in the form of a thin coating on metal [22]). Atomic force microscopy and some other forms of SPM using optical methods, such as sum frequency generation [23] could also be potentially powerful methods for imaging catalytic reactions under gas pressure.

A general and incompletely resolved problem for all in-situ work, other than in SPM, is the possible influence of the electron beam. Atomic displacements are often manifest, for instance in HREM profile imaging of surfaces, but in other cases may still affect the course of any dynamic process even when they are not directly visible. In this respect we have not greatly advanced beyond the early observations of beam-induced dislocation motion.

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