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High Resolution In-situ SEM of Competitive Particle Sintering and Other Surface Processes

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The SEM is a powerful platform for in-situ studies at very high, at more modest and even at low resolution; and in high vacuum and using controlled environments of gas, vapor or actual liquids. The primary advantage of the SEM is the use of robust, inherently stable and representative wide area (millimeters to inches) bulk samples as the primary subject of in-situ study or as substrates. The combination of lateral spatial resolution and chemical and crystallographic analyses is matched by few other surface science methods. Recent advances in imaging methods combine resolutions of almost 1nm at 1kV for imaging with sub-micron, and in some cases near-nm, sensitivities for nanoanalysis. The use of low voltages and digitally processed TV rate scanning separately, or preferably together, generally avoids the previous prerequisite for conductive coating of electrically insulating materials. This is a key development for surface specific in-situ sintering but it is less necessary for modest resolution mechanical deformation and fracture studies in which bulk processes are sampled at the surface which over large areas this may remain unmodified. Ashby et al [1] is a classical example of the latter and we will present data from sintering studies after Jagota et al [2] and Boyes [3] in which the substrate can be either a strong player or just a convenient 2D platform with minimal interactions.

Our current instrumentation utilizes ultra-high resolution FESEMs [3] and in some cases (S)TEMs operated in the SEM mode [2]. Samples are of modest size, which reduces outgassing and contamination issues, and they are mounted in regular TEM hot stages modified to accommodate disks 3mm in diameter and up to >0.5mm thick. These are effectively bulk samples. The in-lens FESEMs conveniently use similar TEM-style stages. In essence we use thicker versions of the disks from which TEM thin sections (the hard part) are typically prepared. This approach allows the high resolution study of much larger components and wider population distributions, and the interfaces between them, than could be accommodated in a TEM thin section. It also allows substrate surfaces to be selected and prepared in ways which are rarely compatible with the preservation of a thin sample. Moreover, on heating or other treatment gross artefact changes in the sample substrate are much less likely to be bothersome, or at least they are more reproducible. We are also developing a reciprocal space shuttle with air outside for the protected transfer of samples into the vacuum or other controlled atmosphere of the microscope [4]. This is designed to protect samples from contamination by transfer through air, including after preparation and evaluation in a UHV, dry box, high pressure liquid reactor or other process environment; and in other applications to protect the environment from people unfriendly samples with poisonous or pyrophoric etc tendencies. A hot stage for polymer sample transformations can be quite simple.

Overall bulk sintering data raise a number of issues which in-situ SEM is used to quantify and to resolve. Our application examples include sintering of soda lime silicate glass spherical beads sieved to <10um size with in some cases metal inclusions of 60Co.28Cr.7Mo of similar or smaller size. We are interested in the effect of constrained sintering between the beads and whether the early mechanisms involve a reduction in the viscosity of the glass by wide metal dissolution or there

is more wetting of the metal by the glass than was initially assumed. Glass wetting of the substrate contributed to the results on Pt but partially graphitized carbon disk [2, 5] substrates supported the various beads without influencing their interactions significantly. It is as though the beads simply float freely and are supported and conveniently constrained by the substrate to a 2D pattern of interactions to observe wetting behavior and measure contact angles between the constituents. The fact that the sintering rate and contact angles are increased with oxidized metal particles and the influence of them in small amounts, together with more direct EDX analysis data, strongly suggest the dissolution model is the cause of the initial increase in sintering rate with metal addition. Low glass metal wetting was observed. At higher levels it is shown the there are strong metal-metal and glass-glass contacts. Unexpected reversible and angle changing glass contacts were also observed in very competitive processes. These mechanisms were studied effectively in the SEM with valuable additional information and a very high productivity for basic parameters compared to ex-situ methods. End point data were comparable by both approaches with an identical onset temperature of 704 (+/-10)^{0}C ex-situ in an air atmosphere DSC furnace and in-situ in the high vacuum SEM. The zero effect of the vacuum in this specific case is attributed to the high oxygen fugacity in the glass beads and to the pre-oxidation of the metal in the most interesting experiments. No influence of the TV rate beam was detected.

Low voltage ultra-high resolution SEM of wide areas containing infrequent substrate attributes are opening up in-situ studies of metal on complex ceramic systems of practical importance. At elevated temperatures conductive coatings are no longer required. The value and productivity of the SEM approach with robust bulk samples is extended when more intense ex-situ reaction conditions are required, e.g. high temperature oxidation or pressurized liquids, although with great difficulty and skill some of this data have also been recorded in the TEM by a number of authors [6]. Finally, the SEM allows direct plan view imaging of surface reactions uncomplicated by underlying bulk microstructures except as they interact with surface data and are therefore relevant. The value of combined in-situ, ex-situ, and other studies cannot be overemphasized.

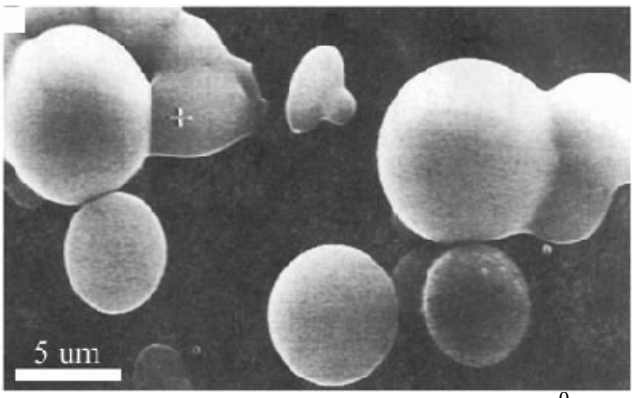

Fig.1 : Impeded glass sintering in-situ at 730^{0}C. Digitally integrated TV rate scanning.

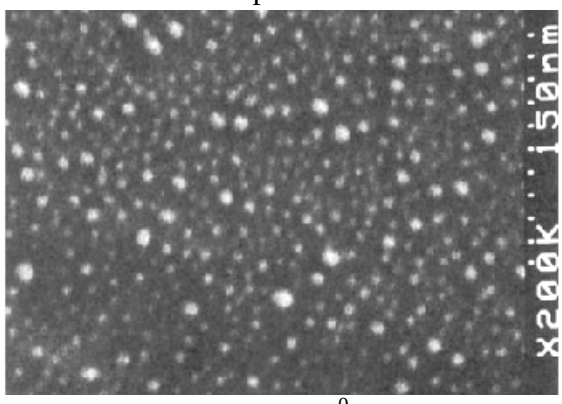

Fig. 2 : Ag on Al_2O_3 at 250^{0}C. 1kV, 200kX In-situ migration and sintering study.

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