Scale dependency of the mechanical response in semi brittle nano particles

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Abstract

Nano based material coating technology is frequently proposed for surface modification. In this context, superior mechanical properties are emphasized with beneficial implications on wear or other tribology aspects. Thus partially, the initial condition for further progress along this avenue remains in the exploration of small volume mechanical behavior. Nano particle properties as a "building block" require better understanding for additional developments or applications. For this purpose, the current paper selected silicon particles in the range of 20–50 nm and mechanical tests were performed at an ambient temperature. Mechanical response assisted by contact mechanic methodology and fine features visualization by novel techniques provided quantitative information to be analyzed. It becomes apparent that scale effect argumentations might assist in explaining the distinction between sufficiently fine segments from bulk properties.

Keywords: silicon, nano scale, contact mechanics, mechanical response.

1 Introduction

Engagement concerning the issue of the actual strength of metallic systems evoked classical considerations particularly vis-à-vis the theoretical values gap. Early investigations [1, 2] emphasized the role of internal or external defects to be dominant variables in shaping or bounding the strength magnitude. With respect to line defects "the whisker" characteristic [3] has been studied introducing significant scale effect on the mechanical response. Studies that intended to modify the material structure in order to achieve unique mechanical properties have been also developed. A relevant example is the field of
amorphous metals [4]. Scale effects as related to mechanical behavior might serve here only a specific example. As known, ample of physical phenomena are size dependent. The role of volume/surface ratio effect is a major issue in solidification and as such involves refinements in order to cope with experimental findings. The current study is centered on sub micron semi-brittle silicon particles with attempt to develop different insights on theoretical/experimental interface. Also, experimental aspects are elaborated since in small volume segments experimental techniques become highly complex. Only with the aid of remarkable developments, that has been associated with novel techniques facilitated quantitative and qualitative information to be gathered regarding the mechanical behavior. This included well controlled monotonic or cyclic in addition to time dependent tests. For more comprehensive analysis, advancement of visualization means with appropriate resolution and computational mechanics provided essential supplements. Due to geometrical constraint, the current study utilized contact mechanics methodology. Note, that nowadays nano indentation procedures enable to establish consistently constitutive material parameters. In elastic-plastic solids the yield strength, plastic behavior, plastic zone, Young modules and fracture resistance become measurable entities. Finally, better understanding of small volume behavior is beyond geometrical argumentation. Due to localization, even macro events might be dominated by a small volume response (ex. processed or micro fractured zones) like fracture and fatigue processes that represent typical examples.

2 Material and experimental procedures

Identified nano spheres of silicon particles in the range of 20-50 nm were selected. The nano particles were synthesized by injecting vapor phase of silicon tetrachloride into argon-hydrogen thermal plasma. The material in this plasma state was then expended through a nozzle to a low pressure, a process that droved the nucleation of silicon nano particles. This synthesis known as hypersonic plasma deposition was then utilized in a focused beam and the nano particles were directed across a sapphire wafer. The substrate was mounted on a computer-controlled translation system and allowed the deposition of nano particles lines. At this stage particles could be accessed with the aid of Scanning Probe Microscope (SPM) based nano indenter. Here, Hysitron Triboscope, Hysitron Inc, Edina MN, USA, was utilized (Fig.1). For remote loading, a diamond of 1000nm tip radius was used at ambient temperature. In fact, the experimental conditions consisted of a diamond indenter with elastic modules of 1100GPa on one side and Al2O3 single crystal substrate with 450GPa modules on the other. Using this set-up implies that the silicon nano particles with a defined geometry was compressed between two relatively rigid platens. The ultra fine particles were also confirmed by selected area diffraction assisted by Philips CM30 Transmission Electron Microscope (TEM) operating at 300KV (Fig.2). In fact, under the current load controlled circumstances the initial deformation was analyzed by contact mechanics methodology.
3 Experimental results

In nano particles of Si with modulus of 170GPa at ambient temperature the scale effect became apparent. Mainly it has been manifested in a consistent trend that
the hardness or strength is size dependent. Smaller size resulted in higher
deformation resistance. For example, the hardness of silicon nano spheres has
indicated a factor of four higher values as compared to <100> bulk silicon. This
behaviour prevailed in testing nano spheres of various dimensions. In the case of
a particle of about 19nm the hardness exceeded by far the aforementioned factor
for a specific load history. With indentations, monotonic or cyclic, information
as related to geometry, displacement and the recovery could be achieved. Particularly the fatigue findings indicated the role of the irreversible strain or the
cumulative value of damage could be measured. This current loading history was
in fact a low cycle fatigue experiment even by considering the frequency
conditions of 0.3 Hz. In spite such limitations, important insights have been
revealed regarding plasticity of silicon at ambient temperature in general and
mechanical behaviour as related to small volume in particular. Some results
concerning cyclic response are demonstrated in figures 3–5.

Figure 3: Load-displacement curves of Si particle.

As depicted, Fig.3 shows the results of repeat loading by a 1µm diamond tip
of silicon nano sphere, deposited on a sapphire substrate. The particle height
prior to each cycle is listed in the right hand column. This particular test was
performed on a particle of original height of 50nm. Load displacement curves for
the first 10 cycles are illustrated in Fig.4.

Hysteresis changes become apparent indicating typical micro plasticity
besides hardening trend. Two SPM images for a Si particle are shown in Fig.5.
On the left, the initial particle of 50nm prior to the imposed load. On the right,
the deformed particle after three cycles at 0.3Hz. The cumulative reversed strain
is determined at each stage of loading by the summed residual displacement (load-displacement curve) as compared to the height change of the specific nano particle (visualization).

4 Discussion

Critical experiments have substantiated already the role of the mechanical size effect. Such experiments in various metallic systems included nano indentation findings, wire torsion and fine sheet bending in terms of hardness, strengths and plasticity behaviour [5, 6]. In fact, the major scale effect as related to mechanical properties is manifested by the increase values of strengths or hardness as the
volume decreases. The mechanical response of small volume segments provides enough incentives for continuous research activities on different levels. Briefly, at least two models have been proposed regarding the length scale effect. First, on the foundation of early work concerning the issue of geometrically necessary and statistically stored dislocation by Ashby [7]. Hutchinson [8] has developed a generalization of the classical plasticity theory. As such, the length scale has been introduced to account for plastic strain gradient effects emerging in deformation at sub micron scale. Following this approach, size effects are attributed to the increasing preponderance of geometry necessary dislocation relative to statistically stored dislocation. This is accentuated in cases in which the scale of the deformation decreases. Second, mainly under indentation the surface to volume ratio approach introduces a length scale by considering this ratio to become a key parameter [9]. As already mentioned the current phenomenological investigation is centred on the mechanical response of ultra fine silicon particles tested under monotonic and cyclic loading at ambient temperature. Beside the significant hardness increase, additional striking results have been noticed. Under the present circumstances of contact stresses, plasticity resulted with substantial strain hardening pattern. Such behaviour by itself is alluding to possible susceptibility to cyclic loading. The role of cumulative damage was experimentally confirmed. Kahn et al. [10] and Komai et al. [11, 12] have addressed the premature failure by fatigue in silicon-based films. Other finding requires additional attention. Silicon has been characterized as a semi brittle system with highly hard Ductile-Brittle transition behaviour that only occurs at about 773K. This means that at lower temperatures dislocation activity is not expected. In contrast, the current findings in silicon single crystal indicate the following sequence of events under imposed load. First, dislocation nucleate, work hardening occurred with a significant back stress. Second, this might result in damage and structural integrity destruction. The nano particles illustrate the scale effect by the properties dependence on the particle size. The case of the nano indentation size effect illustrates also a small volume mechanical response. Here, a typical dependence of the hardness on the penetration depth has been confirmed. The hardness is higher at lower depth reduces to a minimum prior to hardening effects. Generally, the hardness is defined by the imposed load divided by the contact area for a specific indentation tip.

Moreover, under cyclic load by repeated run of indentations, the present super hard nano particles of silicon, indicated changes in the hysteresis pattern. In this context, the displacement consisted in a partition nature of reverse and irreversible plastic strain. This partition that could be approached quantitatively actually indicated that plastic behaviour was size dependent. In some cases the load-displacement curve enabled to track a staircase yield excursions attributed to dislocations injection. The origin mechanism that might cause hardening as well as cumulative damage becomes apparent. Here to mention the argument, that in brittle material, fatigue occurs by cycle dependent degradation of the extrinsic toughness in the wake of the crack tip. Accordingly, cyclic loading or friction wear degradation is attributed to the reduction of the extrinsic crack tip shielding [13, 14]. Nevertheless, under contact mechanical methodology
dislocation mobility occurs and the argumentation of native oxide initiation sites or dynamic environmentally enhanced fracture is not decisive. Contact test under load-controlled conditions requires special attention to the remote applied stress values. Variation of the contact area modifies the average stress and changes the applied stress amplitude. Kobayashi et al. [15] investigated deformation of Al2O3 single crystals under repeated indentation. The study concluded that analogy of the sapphire response to the conventional S-N fatigue curves in metallic system could be deducted. Even in ceramic materials, plasticity occurs and above some thresholds twinning has been observed with crystallographic habits. Thus, in addition to well-established view regarding the thermal role in silicon, even at ambient temperatures semi ductile behaviour resulted. This means, that a more comprehensive view must include also the role of the state of load, constraint circumstances on top of thermal activation factors. The aforementioned issue remains important not only regarding the scale factor but also to structural integrity aspects of small volume systems. A summary of the aforementioned research activity is in order. In small volume problems, length scales are introduced in order to predict deformation behaviour and strength. In this framework also the indentation size effect has been focused representing in fact small volume response in the nano scale. Thus, mutual arguments were adopted from general plasticity concepts up to specific test conditions. The surface to volume ratio approach emerged from atomic model simulation and remains consistent for shallow indentation depth below 100nm and requires a case-by-case assessment confined to the experimental conditions. This approach resulted in hierarchy of length scales similar to the continuum plasticity approach.

Figure 6: Stair-case yielding in a 39nm diameter particle.
5 Conclusions

1. Silicon nano spheres in the 20-50nm radii range, the hardness increased to 50 GPa as compared to values of about 10GPa for silicon bulk.
2. Super hard behaviour under indentation beside other procedures raises the issue of the length scales as related to mechanical response.
3. At ambient temperatures a semi brittle behaviour occur indicating work hardening and thus, cyclic damage susceptibility.
4. Dislocation activity model can provide clarification to the experimental findings.

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References