Mechanical Properties of Nanomaterials: A Review

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Abstract

This paper reviewed the literature highlight the mechanical properties of nanomaterial and mention why the world attracted to the Nanomaterials. Nano-structured and Nanoparticle based materials exhibits unique microstructures and enhanced mechanical performance. That uniqueness attracted considerable attention in recent years and offer interesting possibilities related to many structural applications. The day by day increasing applications of nanomaterials in different perspectives have produced a positive impact on researchers and hence efforts are now being carried out to study the mechanical properties of the nano-structured materials. Therefore, it is an important topic of research nowadays. The present review emphasises the study of mechanical properties primarily tensile and compressive behavior of nano-structured materials at room temperature, the influence of the nano size of the particles on the creep behavior of nano materials

Key Words: *Creep Behavior, Advanced Material, Nanomaterials, Mechanical Properties.*

INTRODUCTION:

Nano-Particles are particles with at least one dimension smaller than1 micron and potentially as small as atomic and molecular length scale ((~0.2 nm). Nanoparticles can have amorphous or crystalline from and their surface can act as carrier for liquid droplets or gases. To some degrees, nano-particulate matter can be considered a distinct state of matter in addition to the solid, liquid, gaseous, and plasma states, due to its distinct properties (large surface area and quantum size effects) [1]. New discoveries of unique properties of some nanoscale materials attracted the attention of whole world. While inspecting the microstructures with the optical microscope, it was recongnised that refined microstructures often provided attractive properties such as increased strength and toughness in structural materials. Example of property enhancement due to a refined microstructure was age hardening of aluminum alloys.

The ultra small size (<100 nm) of grains in these nanostructured materials can result in dramatically improved of different properties from conventional grain size (>1 μm) of same chemical composition. These properties represent the subject of multidisciplinary research efforts motivated by the wide range of their applications in high technologies.

Today, we can say with no doubt that nanostructured materials emerging as future with unique combination of high strength and superplasticity represents ideal materials for a wide range of applications in aerospace and automotive industries, medicine, energy etc. But to develop these materials for high technology and to achieve progress in the fundamental science of nanostructures, it is important to understand the underlying properties of these materials under different environments.

While there are numerous properties that may be dramatically changed when the microstructure is nanoscale, the main aim of this paper is to give a brief overview on those which the recent work with nanostructured materials has been most extensive that is the mechanical properties of nanostructured materials such as elastic properties, ductility and toughness, hardness and strength, creep behavior, etc.

Mechanical Properties of Nanostructured materials:

The nano scale size of the nanomaterials tends to modify many of the mechanical properties of nanostructured materials from the bulk materials. An enhancement of mechanical properties of nanomaterials generally results from structural perfection of the materials [3]. Particles size reduction to nano-meter scale poses new technological challenges such as particle agglomeration and de-bonding from matrix. The role of atomic-scale forces of Van der Waals attraction and electrostatic repulsion must also be taken into account to fully understand the mechanics of particles interaction. Improvements in mechanical property have resulted in major interest in nano composite in various automotive and general industrial applications. [4].

Elastic Properties:

Early measurements performed on nanostructured materials prepared by gas condensation method depicted lower values of the elastic constants like Young's modulus as compared to the values for conventional grain size materials. While many reasons were attributed for the low values of E, Kristc and coworkers [5] suggested that the presence of extrinsic defects such as pores and cracks were responsible for the low values of E in nanostructured materials compacted from powders. However, Wong et al. [6] observed that nanocrystalline Nickel powder produced by electroplating with negligible porosity levels had an E value comparable to fully dense conventional grain size Nickel. Subsequent work on porosity-free materials has supported these conclusions, and it is now believed that the intrinsic elastic moduli of nanostructured materials are essentially the same as those for conventional grain size materials until the grain size becomes very small, less than 5 nm. This is illustrated in Figure 1 for nanocrystalline Fe prepared by mechanical attrition and measured by a nano-indentation technique.
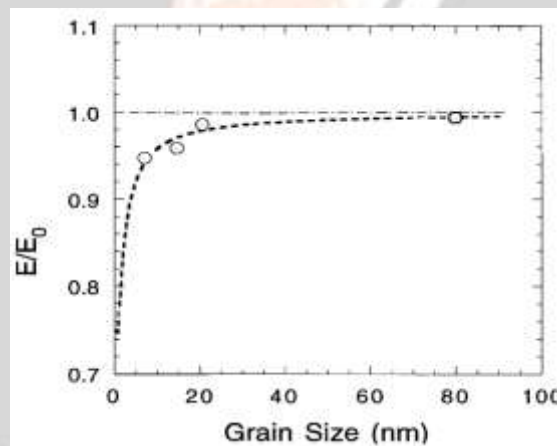

Figure 1: Plot of the ratio of Young's modulus E in nanograin iron to its value E_o in conventional granular iron as a function of grain size.

Hardness and Strength:

Among many of the novel mechanical properties of nanostructured materials, high hardness has been discovered from many nanostructured materials system. A variety of superhard nanocomposites can be made of nitrides, borides and carbides by plasma-induced chemical and physical vapor deposition [7]. In the appropriately synthesized systems, the hardness of the nanocomposite exceeds significantly than that of mixtures in bulk. Superhardness also comes from pure nanoparticles. For example, Gerbericha report the superhardness from the nearly spherical, defect-free silicon nanospheres with diameters from 20 to 50 nm of up to 50 GPa, fully four times greater than the bulk silicon [8].

Hardness and strength of conventional grain size materials (grain diameter, d > 1 μm) is a function of grain size. The dependence of yield stress on grain size in metals is well established in the conventional polycrystalline range (micrometer and larger sized grains). Yield stress, σ_y for materials with grain size d, is found to follow the Hall–Petch relation:

$$\sigma_y = \sigma_0 + kd^{-1/2} \qquad\qquad (1)$$

where σ_0 the friction stress apposing dislocation motion and k is is a constant. This indeed an approximation, and a more general formulation is to use a power expression with exponent –n, where $0.3 \leq n \leq 0.7$.

To explain these empirical observations, several models have been proposed, which involve either dislocation pileups at grain boundaries or grain boundary dislocation networks as dislocation sources.

Several recent reviews have summarized the mechanical behavior of these materials (Siegel and Fougere [9]; Siegel [10]; Morris and Morris [11]; Weertman and Averback [12]). It is clear that as grain size is reduced through the nanoscale regime (< 100 nm), hardness typically increases with decreasing grain size and can be factors of 2 to 7 times harder for pure nanostructured metals (10 nm grain size) than for large-grained (> 1 µm) metals.

The experimental results of hardness measurements, show different behavior for dependence on grain size at the smallest nanocrystalline grains (< 20 nm), including

    a) A positive slope ("normal" Hall-Petch behavior),
    b) ~ Zero slope (essentially no dependence), and
    c) A negative slope (Siegel and Fougere [9]; Siegel [10]; Morris and Morris [11]; Weertman and Averback [12]).

Most data that exhibit the negative Hall-Petch effect at the smallest grain sizes have resulted from nanocrystalline samples that have been annealed to increase their grain size. Only a few cases of negative Hall-Petch behavior have been reported. These include electrodeposited nanocrystalline alloys and devitrified nanocrystalline alloys (Erb et al [13]; Alves et al. [14]). It is suggested that thermally treating nanophase samples may result in such changes in structure as densification, stress relief, phase transformations, or grain boundary structure, all of which may lead to the observed negative Hall-Petch behavior (Siegel and Fougere [9]). Nanocrystalline thin films with grain sizes ≤ 6 nm are also observed to exhibit a negative Hall-Petch effect (Veprek [15]).Thus it seems likely that in many cases the observed negative Hall-Petch slopes are due to artifacts of the specimen preparation methods.

Ductility and Toughness:

In the conventional grain size (> 1 µm) regime, usually a reduction in grain size leads to an increase in ductility. Thus one should expect a ductility increase as the grain size is reduced to nanoscale. On a very basic level, mechanical failure, which limits ductility, is an interplay or competition between dislocations and cracks (Thomson [16]).Nucleation and propagation of cracks can be used as the explanation for the fracture stress dependence on grain size (Nagpal and Baker [17]). Grain size refinement can make crack propagation more difficult and therefore, in conventional grain size material, increase the apparent fracture toughness. However, the large increases in yield stress (hardness) observed in nanocrystalline materials suggest that fracture stress can be lower than yield stress and therefore result in reduced ductility. Koch [18] identified three major sources of limited ductility in nanocrystalline materials, namely:

    1. Artifacts from processing (e.g. Pores);
    2. Tensile instability;
    3. Crack nucleation or shear instability.

The results of ductility measurements on nanocrystalline metals are mixed and are sensitive to flaws and porosity, surface finish, and method of testing (e.g., tension or compression testing). In tension, for grain sizes < 30 nm, essentially brittle behavior has been observed for pure nanocrystalline metals that exhibit significant ductility when the grain size is conventional.

Figure 2(a) shows data on normalized yield strength (strength/strength of conventional polycrystalline) versus percent age elongation in tension for metals with grain sizes in the nanocrystalline range. There is a clear decrease in ductility as strength is increased. By comparison, ultrafine grained materials (100–500 nm), Figure 2(b), exhibit increased yield strength along with good ductility in comparison to nanograined materials.
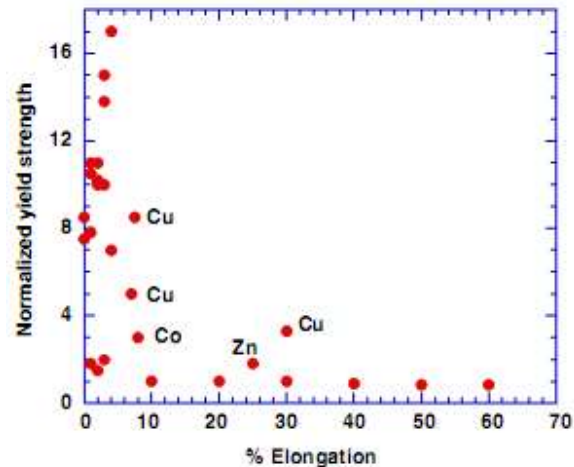
Figure 2(a): Compilation of yield stress verses elongation showing the reduced ductility of nanocrystalline metals [18].
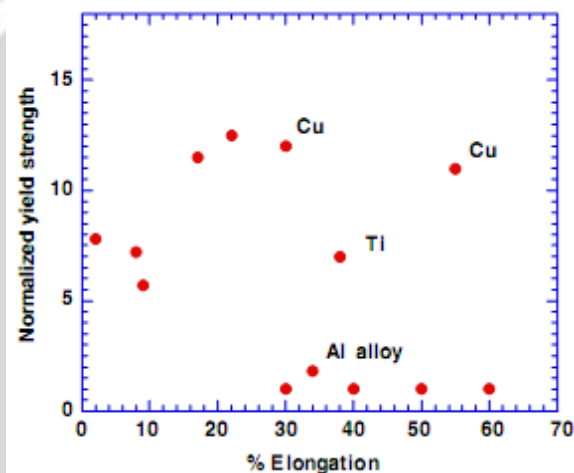

Figure 2(b): Compilation of yield stress verses elongation of various ultrafine grained metals [19].

Zhang et al. [20-22] varied the microstructure of nanostructured / ultrafine grain size of Zn by changing the milling times. A very dramatic modulated cyclic variation of hardness was observed as a function of milling time at liquid nitrogen temperature. The sample cryomilled for 4 hr exhibited an optimal combination of strength and ductility. The grain size distribution in this sample contained 30% volume fraction of grains larger than 50nm along with the smaller nanoscale grains. This sample which exhibits more strain hardening than samples milled for either shorter or longer time, combined the strengthening from the reduced grain size along with the strain hardening provided by dislocation activity from larger grains.

Non equilibrium grain boundaries [23] have also been proposed as a mechanism to enhance ductility. It has been argued that such boundaries provide a large number of excess dislocations for slip [24] and can even enable grains to slide or rotate at room temperature, leading to a significant increase in the strain hardening exponent. Another way of increasing ductility is to decrease the strain rate in order for the specimen to sustain more plastic strain prior to necking [25]. The increased ductility that is exhibited in some cases comes, basically, from the inhibition of shear localization.

Creep of nanocrystalline materials:

Creep in coarse grained materials has been widely studied for approximately one century and accurate models exist to capture deformation features and to explain mechanisms involved therein. Creep in nanocrystalline materials has been studied only in recent years owing to several complications involved.

I.   The limitation of synthesizing bulk nanomaterial free of defects (porosity and impurities) with uniform grain size distribution that could provide reliable data to explain the deformation process.

II.   The significant increase in the volume fraction of grain boundaries and intercrystalline defect s such as triple lines and quadruple junctions that renders the creep mechanism complicated and leads to associated challenges in developing a model that could explain the deformation process.

III.   Grain growth occurs at much lower temperature as compared to coarse grained materials limiting the testing temperatures to a low fraction of the melting point.

Diffusion creep is considered to be significant because the volume fraction of grain boundaries is high. Bird -Dorn-Mukherjee had given an equation for the high temperature deformation of crystalline materials which is

$$\dot{\varepsilon} = \frac{ADGb}{kT}\left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \qquad\qquad (2)$$

where $\dot{\varepsilon}$ is the strain rate, A is a dimensionless constant , G is the shear modulus, b is the magnitude of the Burgers vector, k is Boltzmann's constant, T is the absolute temperature, p is the inverse grain size exponent, and n is the stress exponent. Among the established diffusion creep mechanisms in coarse grained materials are

1.   The Nabarro-Herring creep that involves vacancy flow through the Lattice, the related equation is

$$\dot{\varepsilon}_{NH} = \frac{A_{NH} D_L Gb}{kT}\left(\frac{b}{d}\right)^2 \left(\frac{\sigma}{G}\right) (3)$$
where D_L is the lattice diffusion coefficient, p=2, n=1, and the dimensionless constant A_{NH}=28.

2.   Coble creep that involves vacancy flow along the grain boundaries, the related equation is

$$\dot{\varepsilon}_{CO} = \frac{A_{CO} D_{gb} Gb}{kT}\left(\frac{b}{d}\right)^3 \left(\frac{\sigma}{G}\right) (4)$$
where D_{gb} is the grain boundary diffusion coefficient, the exponents p=3, n=1, and the dimensionless constant A_{CO}=33

Palumbo et al. [26] considered a regular 14-sided tetrakaidecahedron as the grain shape to estimate total intercrystalline component and showed that it increases from a value of 0.3% at a grain size of 1 μm, to a maximum value of 87.5% at a 2 nm grain size (Fig. 3).
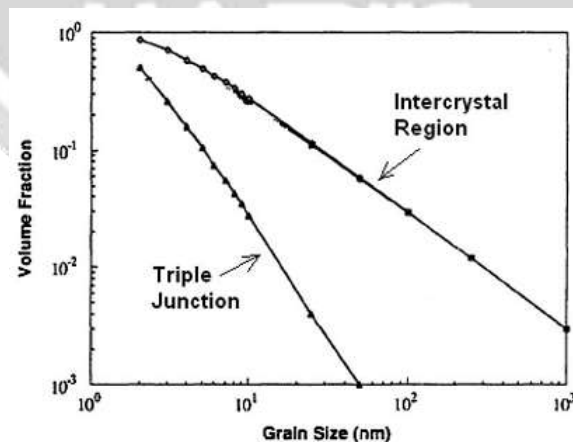

Figure 3: The effect of grain size on calculated volume fractions of intercrystal regions and triple junctions, assuming a grain boundary thickness of nm [25]

It was noted that the triple junction volume fraction displays greater grain size dependence than grain boundary. Wang et al. [27] modified the standard diffusion creep equation to accommodate for diffusion along triple lines and this leads to the following express ion for triple-line diffusion creep:

$$\dot{\varepsilon}_{TL} = \frac{A_{TL}D_{TL}}{kTd^4}\Omega\delta^2\sigma \tag{5}$$

where A_{TL} is a constant depending on the geometry and boundary conditions, D_{TL} is the triple- line diffusion coefficient, Ω is the atomic volume and δ is the grain-boundary width.

Chokshi [29] proposed the following form for the Bird–Mukherjee –Dorn equation (Eq. (2)) for conditions under which transition takes from one diffusion creep mechanism to the other and also from diffusion controlled mechanism to intergranular dislocation power law creep:

$$\dot{\varepsilon}_{PL} = \frac{AD_L}{kT}\left(\frac{\sigma}{G}\right)^n \tag{6}$$

where n ≥ 3, p = 0 and D = D_L in the Bird–Mukherjee–Dorn equation. Wang et al. [30] attributed the creep response to grain-boundary diffusion and in their following work [31] concluded that while grain- boundary diffusion is the operating mechanism in nanocrystalline creep; a combined mechanism involving dislocation creep an d grain- boundary diffusion governs deformation in coarse grained materials. In Fig. 4(a), one can see that the slope of the plot, n = 1, supports either Coble or Nabarro– Herring creep (Eqs. (3) and (4)). Hahn et al. [31] performed tests on compressive creep response of TiO. The value of n obtained from their results is shown from the slope in Fig. 4(b): n = 2.

Nieman et al. [32] reported no significant room temperature creep for nanocrystalline Pd under loads much larger than the yield stress of a coarse-grained Pd sample. They concluded that grain boundary diffusional creep is not an appreciable factor in directly determining room temperature mechanical behavior in nanocrystalline Pd. Sanders et al. [33] carried out creep tests over a range of temperatures (0.24– 0.64T_m) and stresses on samples of nanocrystalline Cu, Pd, and Al–Zr made by inert gas condensation and compact ion. The experimentally observed creep rates were two to four orders of magnitude smaller than the values predicted by the equation for Coble creep. The predicted creep rates as a function of temperature for different grain sizes are shown in Fig. 5.
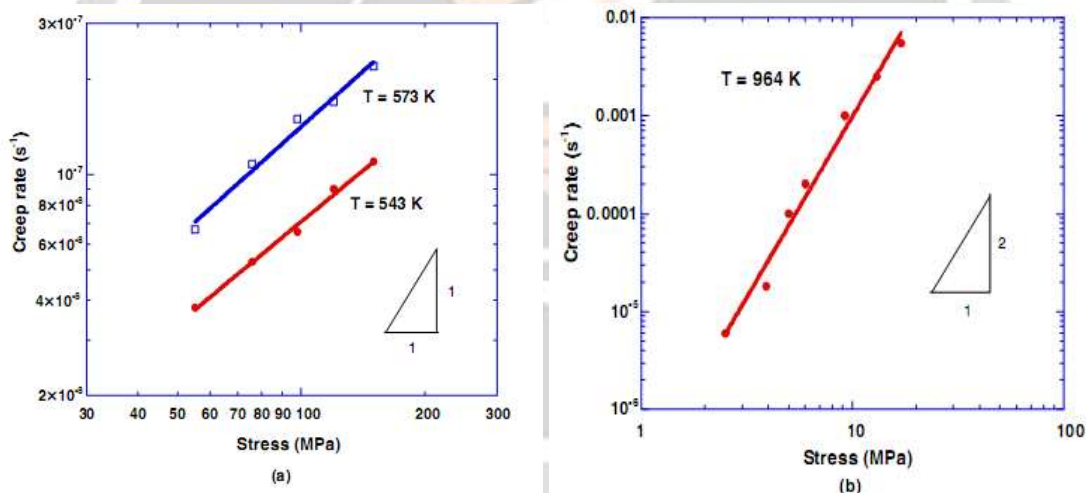

Figure 4: Stress versus strain rate plots for (a) nanocrystalline (d=28 nm) NiP[29] and (b) nanocrystalline Tio$_2$[31]
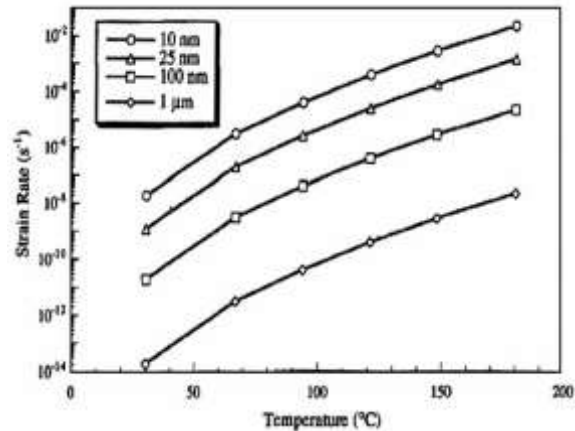
Figure 5: Calculated creep curves assuming grain-boundary diffusion for different grain sizes; notice increase in strain rate by six orders of magnitude when grain size is decreased from lμm to10nm [33].

The figure shows calculated creep curves assuming grain-boundary diffusion for different grain sizes (notice increase in strain rate by six orders of magnitude when grain size is decreased from lμm to10nm). Sanders et al. [33] concluded that prevalence of low-energy grain boundaries together with inhibition of dislocation activity caused by small grain sizes is responsible for low strain rates and higher than expected creep resistance

Conclusions:

This paper reviews the mechanical properties of nanocrystalline materials, focusing on the fundamental physical mechanisms responsible for the specific behaviors. The main conclusions outlined by reviewing the extensive literatures.

a) *Grain-boundary structure:* There is no evidence that the grain boundaries in nanostructured materials are significantly different from the ones in conventional polycrystals. One can assume safely a boundary a few atomic distances thick. However, it is safe to assume that the number of grain-boundary ledges is reduced because of the size. The reorientation/rotation of the nanosized boundaries is also significantly enhanced in comparison with conventional boundaries.

b) *Yield stress:* The yield strength of nanocrystalline materials has been measured and there is a consensus that the H–P relationship breaks down with a decrease in slope in the 1μ m–100 nm range.

c) *Ductility:* Nanocrystalline metals are characterized by a low work-hardening rate, which is a direct consequence of the low density of dislocations encountered after plastic deformation. This low work hardening rate leads to tensile instability and a low tensile ductility. There are reports of increased ductility in nanocrystalline metals; the increased ductility that is exhibited in some cases comes, basically, from the inhibition of shear localization.

d) *Creep:* There are several studies in the literature, reporting a decrease in creep resistance by virtue of Coble creep in which the creep rate is proportional to d^{-3}. Nevertheless, conflicting results report a creep resistance much higher than the Coble prediction. This could be due to the contamination of the grain boundaries with impurities, which act as "brakes" to grain-boundary sliding.

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