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Original Research Paper

Unusual higher viscosity for nanocrystalline titanium powders: Compared to micron titanium powders

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ABSTRACT

We adopted the verified absolute-reaction theory which originates from the quantum chemistry approach as well as the boundary perturbation technique to capture the unusual experimental results by Dabhade et al.: Nanocrystalline titanium powders were found to exhibit lower activation energy for viscous flow and higher (coefficient of) viscosity as compared to micron sized titanium powders when nanocrystalline Ti (micron and nano) powders were expected to exhibit viscous flow during sintering. We also illustrate some formulations which can help us calculate the temperature-dependent viscosity of flowing Ti powders in micro- and nanodomains.

1. Introduction

According to their characteristic length-scales in the range of a few, and up to hundreds of nanometers, nanopowders have a potential interest for technological applications due to e.g. their electronic, magnetic, and optical properties. Titanium (Ti) is used in many applications, ranging from aerospace engineering to chemical processing as well as medical technology. Unalloyed commercially pure Ti has advantages such as corrosion resistance, inertness and biocompatibility over commonly used Ti alloy. However, the use of commercially pure Ti has been limited due to its relatively low strength [1–3]. One of the approaches available for improving the strength of commercially pure Ti is the refinement of the grain size. According the Hall-Petch relationship, decreasing grain size should lead to increasing yield strength. Numerous experimental investigations have demonstrated that the strength and hardness of metals with ultra-fine grains (100 nm < grain size < 1 μm) or nanocrystalline grains (grain size < 100 nm) are significantly enhanced over those of their coarse-grained counterparts.

Since its introduction into modern science as a major field by Gleiter, ultra-fine grain and nanocrystalline grain materials have been the subject of widespread research [4]. Nanocrystalline materials, including nanocrystalline powders exhibit two kinds of atomic ordering, the crystal atoms which are ordered and the boundary atoms which are disordered. The influence of boundary atoms or disordered atoms increases with the decrease in the crystallite size; thus the behavior of nanocrystalline powders is often dominated by events at the grain boundaries [1–3]. During sintering, nanocrystalline powders are likely to exhibit viscous flow due to the presence of these disordered atoms (amorphous region) at the grain boundaries. The role of viscous flow during sintering of nanocrystalline powders is still not clear [3].

In fact titanium is a complex system as regards sintering/diffusion studies. Titanium powder has an oxide film on its surface which is stable and influences the sintering process [1–3]. Titanium transforms from room temperature alpha to high temperature beta phase that leads to formation of dislocations. The latter could play a role in sintering. Due to its allotropic nature titanium exhibits different diffusivities in the α-Ti (hcp) and β-Ti (bcc) range (bcc metals due to their less closed structure exhibit larger diffusion coefficient than that with a hcp structure which is close packed). Due to its unusually large ionic to atomic radius hcp-Ti can dissolve impurity atoms interstitially (which in normal case would have dissolved substitutionally) that subsequently diffuse by interstitial mechanism.

Dabhade et al. performed some experiments to fix the contribution of viscous flow during sintering of micron sized and nanocrystalline titanium powders [2,3]. Interestingly they found an unusual behavior: Nanocrystalline titanium powders exhibit

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Nomenclature

a	mean-averaged outer radius	ϵ	(small) amplitude of the (wavy) corrugations
h	Planck constant	κ	distance the patch moves per jump)
K_0	dimensionless constant	κ_1	distance between moving layers of particles
k	wave number of the corrugations	$\kappa_2\kappa_3$	dimensions of unit of flow in the direction of flow and perpendicular to the direction of flow
k_B	Boltzmann constant	$\dot{\Omega}$	shear strain rate
L	wave length of the corrugations	$\dot{\Omega}_0$	(referenced) shear strain rate
$\mathbf{n}$	unit normal (vector)	ψ	dimensionless forcing parameter
r	space coordinates	τ	shear stress
T	absolute temperature	τ_0	(referenced) shear stress
V_m	flow volume $\equiv\kappa_2\kappa_3\kappa_1$	θ	(orientation) coordinantes
V_A	activation volume	ν_0	frequency
v	deformation rate or velocity		
$\mathcal{F}$	activation energy		

lower activation energy for viscous flow and higher coefficient of viscosity as compared to micron sized titanium powders [3]. In this short paper we shall adopt the verified transition-state theory or absolute reaction theory [5–8] together with the boundary perturbation technique to capture this unusual behavior considering the microscopic environment under high temperature regime.

As evidenced in [5,8,9] and presented below our microscopic approach can capture the critical temperature-dependent viscosity transition of microscopic Ti powders in nanodomains as well as the scale-dependent effects by tuning the activation energy and activation volume. Meanwhile it is easy to apply our approach to relevant external field-driven problems [10–13] and other interesting issues [14–17].

2. Theoretical formulations

We shall investigate the temperature-dependent Ti (powder) viscosity in micro- and nanodomains (presumed to be cylindrical) by using the verified absolute reaction theory [5–8] which originates from the quantum chemistry approach. In fact according to Eyring's idea: A shearing force is applied across the two layers of particles or atoms, and (viscous) flow takes place when a single particle or atom squeezes past its neighbors and drops into a vacant equilibrium position (a hole or defect) at a distance, κ, from its original position [5–8]. We remind the readers that our approach for the flow properties of the Ti (micron and nano) powders is essentially a more realistic nonlinear flow law. From the Eyring's absolute reaction model [5–8] (considering the stress-biased thermal activation), structural rearrangement is associated with a single energy barrier (height) $\mathcal{F}$ that is lowered or raised linearly by a (shear) yield stress τ. If the transition rate is proportional to the shear strain rate (with a constant ratio: $K_0 \approx 2V_A/V_m$), we can calculate the shear stress [5–8]

$$\tau = 2\left[\frac{\mathcal{F}}{V_A} + \left(\frac{k_BT}{V_A}\right)\ln\left(\frac{2\dot{\Omega}}{K_0\nu_0}\right)\right], \tag{1}$$

where V_A is the activation volume, $\dot{\Omega}$ is the shear strain rate, ν_0 is an attempt frequency [5–8], e.g., for temperatures (T) being $O(1)$ K (kelvin): $\nu_0 \approx k_B/h \sim O(10^{11})$ (1/sec) with k_B being the Boltzmann constant and h the Planck constant. Normally, the value of $V_A(\equiv \kappa_2\kappa_3\kappa)$ is associated with a typical volume required for a microscopic shear rearrangement (κ is the distance the patch moves per jump). Here $V_m = \kappa_2\kappa_3\kappa_1$, κ_2 κ_3: dimensions of unit of flow in the direction of flow and perpendicular to the direction of flow (the directions of κ_2 and κ_3 both being perpendicular to that of κ_1) and κ_1 is the distance between moving layers of particles [5] (cf. Fig. 1).

We consider a steady, fully developed transport of the (micron or nano) Ti powders under high loading in a wavy-rough tube-like confined domain of a (in mean-averaged outer radius) with the outer interface being a fixed wavy-rough surface: $r = a + \epsilon\sin(k\theta)$ where ϵ is the amplitude of the (wavy) roughness and k is the wave number: $k = 2\pi/L$ (L is the wave length). We can have (via the boundary perturbation series method [9]), after using the forcing parameter

$$\psi = -\left(\frac{a}{2\tau_0}\right)\left(\frac{dp}{dz}\right) \tag{2}$$

($\tau_0 = 2k_BT/V_A$ and dp/dz being the external forcing along the axis of the cylindrical domain or the transport direction)

$$\dot{\Omega} = \dot{\Omega}_0\sinh(\psi) + \text{HOT} \tag{3}$$

with the small wavy-roughness effect being the first order perturbation which is rather small and thus neglected (HOT means the higher order contributions [9]). Here the shear rate ($\dot{\Omega}$) is obtained by

$$|\dot{\Omega}| = \left|\frac{dv}{dn}\right| = |\nabla v\cdot\mathbf{n}| = \left[1+\epsilon^2\frac{k^2}{r^2}\cos^2(k\theta)\right]^{-\frac{1}{2}}\left[v_r|_{(a+\epsilon dr,\theta)} - \epsilon\frac{k}{r^2}\cos(k\theta)\,v_\theta|_{(a+\epsilon dr,\theta)}\right]. \tag{4}$$

with $\mathbf{n} \equiv \nabla[r-a-\epsilon\sin(k\theta)]/|\nabla[r-a-\epsilon\sin(k\theta)]|$ being the unit normal of the general interface [9] which is between the confined (micron or nano) Ti powders and the environment. The temperature-dependent (referenced) shear rate [5–9] is

$$\dot{\Omega}_0 = 2\left(\frac{V_A}{V_m}\right)\left(\frac{k_BT}{h}\right)\exp\left(\frac{-\mathcal{F}}{k_BT}\right), \tag{5}$$

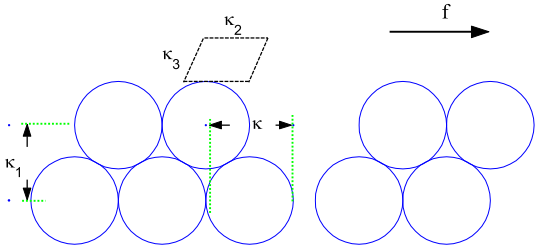

Fig. 1. Schematic plot of an Eyring's flow. Eyring proposed [5] that shear occurs along sets of parallel planes. The distance between these planes is indicated by the symbol κ_1. The shear force per unit area is indicated by **f**. A patch of atoms or molecules whose cross-sectional area is $\kappa_2\kappa_3$ shift or jump as a unit on either side of the shear plane. The distance the patch moves per jump is κ.

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