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Temperature dependence of ceramics hardness

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Abstract

While the hardness of ceramics is well known to be a function of temperature, the present study will investigate the dependence of hot hardness on ceramics density . Ceramics with different composition, bonding and structure show similar hardness behavior in terms of energy density characteristic. Degradation in hardness with increasing temperature correlates well with thermal expansion behavior, so that materials with larger thermal expansion coefficients are expected to soften as their temperature rises. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

1. Introduction

Ceramics materials are favoured for high-temperature applications because of their high melting point, chemical stability, stiffness and strength. The design and development of structural high-temperature materials such as cutting tools thus must take into account the temperature dependence of the material mechanical properties. Diamond tip indentation hardness measurements offer a convenient, nondestructive means of strength probing and can be extended to high temperatures. Small samples can be tested by this method, and the results are relatively insensitive to macroscopic defects, which can significantly affect the tensile strength, or even the elastic properties, of a material. Hot hardness tests have been used to evaluate the high-temperature strength of various ceramics materials including oxides, nitrides and carbides [1–10]. The hardness data considered for the present study show a decrease in hardness as temperature increases. In most of the studies, the data was fitted by a functional relationship of the form

$$H = H_o e^{-aT} \tag{1}$$

where H_o and a are constants determined from the experimental data, and T is the test temperature (°C). The values of those constants are summarized in Table 1 [9,11]. Ceramics hardness should be a function of temperature, but the function shown in the present study is fitted for purposes of calculation and has no relevance to physical behavior.

Lankford [7] measured hardness H and compressive strength σ_c of several structural ceramics, including Al_2O_3, SiC and Si_3N_4, from room temperature (RT) to 1000°C. Those two properties showed qualitatively similar tendencies at temperatures as high as $T/T_{mp} \approx 0.5$, and the temperature dependence of both H and σ_c were rationalized on the basis of thermally activated plasticity and temperature-controlled changes in the tensile microfracture mechanisms. The explanations for these observations are all qualitative, but want of any quantitative relation.

Hillig [9] reasoned that the stiffness and strength of oxides should reflect the strength of the chemical bonding between the metal cations and the oxygen anions. For the paucity of direct information regarding high-temperature mechanical/elastic properties, the cationic field strength was used as a semiquantitative basis for estimating such properties for oxide materials and the hot hardness also was measured as a guide to mechanical behavior. Various elastic constants were correlated with the the field strength of the cationic species, and, the apparent atomic volume of oxygen V_o. The V_o value was determined from crystallographic data, and the relation between room-temperature hardness and Vo was expressed as

$$H = 5.55 \times 10^4 / V_o^{3.8}\ GPa \tag{2}$$

The correlation between H and V_o accorded with the expectation that the interatomic binding forces would

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affect hardness; departures of the measured values from the calculated function line showed that other factors, such as dislocation mobility, play a major influence. Hot hardness data, as well as physical properties, for some oxides are also given in Table 1.

Hard materials generally are modelled by a deep potential energy well with steep walls. Those characteristics imply a combination of high cohesive energy and short bond length. Ohring [12] divided the cohesive energy by the molar volume of the materials and showed that high lattice energy density leads to hard material. Gilman [3,13,14] demonstrated that hardness can be calculated as energy density. He found that, in the case of refractory carbides and biborides, the excess binding energy associated with metal-metalloid interactions must be overcome for a dislocation to move through the crystal structure. Taking this necessity into account, hardness can be expressed as a simple function

$$H \approx -2\Delta H_f / V_m \tag{3}$$

where $(-\Delta H_f)$ is the heat of formation at STP(standard temperature and pressure, 0°C, 1 atm) and V_m is the molecular volume. Good agreement among measurements was found for some representative compounds.

2. Study method

The hardness data investigated for the present study were taken from works of Ref. [1–11]. Since energy density is considered a basis of hardness, at low homologous temperature ($<0.5\ T_{\mathrm{mp}}$) and in the absence of phase transformation, the influence of thermal expansion on hot hardness could be evaluated. For simplification, the average linear thermal expansion coefficient (CTE) values was used in the present work. Using the linear CTE and the room temperature (RT) density value to calculate the densities at various temperature, the correlation with hardness could be determined.

Table 1
Physical properties and hot hardness data ($H = H_o e^{-aT}$) of some ceramics (from Kramer [11] and Hillig [9])

Material	Density (g/cm^3)	CTE (10^{-6}/K)	H_o (kg/mm^2)	a (10^{-4}/°C)	Temperature range (°C)
TiC	4.9	8.3	3300	18.3	0–1000
ZrC	-	6.93	3000	16.4	0–1400
HfC	12.3	6.6	3000	14.7	0–900
NbC	-	6.8	2400	15.3	0–1400
TaC	14.5	7.1	1800	6.75	0–540
WC	15.7	4.0	2350	3.62	0–720
SiC	3.22	5.3	3350	10.5	0–1300
TiN	5.4	9.3	2100	23.5	0–1000
HfN	-	6.9	2000	8.57	0–1000
Si_3N_4	3.19	5.3	1900	2.79	0–400
Al_2O_3	3.98	6.5	2300	7.85	0–800
BeO	3.01	9.4	900	18.85	0–800
$BeAl_2O_4$	3.69	6.2–6.7	1880	7.85	0–900
Mullite	3.38	5.5	1550	4.09	0–1000
TiB_2	4.5	7.8	3500	18.9	0–1000

3. Results and discussion

As shown in Figs. 1–4, hot hardness clearly is a function of mass density, and a near linear relationship can be constructed . The available hot hardness data are limited, and measured values depend on the apparatus used, the volume fraction and size distribution of porosity, and the purity, stoichiometry, and grain size of the specimens. The data cited for any specific material, however, were all taken from the same work, so the results are not so disturbed. Whatever the differences in composition, bonding and structure among the materials tested, the same tendency was observed: Hot hardness was dependent on the density of the material.

Hardness represents not only an entire complex of mechanical properties, but, at the same time, a measure of the intrinsic bonding of a material. Obviously, hard materials have highly covalent bonds, and increasing the ionic character of a bond leads to reduced hardness. In regard to the hardness anisotropy of ceramics, the effective resolved shear stress dominates the hardness measured on various planes and directions of a single crystal [15], which confirms the correlation between hardness and slip behavior. Depending on the material, such properties as cracking, viscous flow, slip and densification may be involved in measuring indentation hardness. That involvement implies that a single factor cannot describe the intrinsic hardness of ceramics, however, like the effective resolved shear stress to anisotropy of hardness, some factors do dominate for a specific case.

It has been established that plastic deformation is controlled by a thermally activated process [16]. Excluding the influence of equivalent effective stress at the activation site, the true activation energy represents that energy needed to overcome the barrier when a dislocation segment or a vacancy moves. Dieter [17] showed the dislocation velocity is a strong function of shear stress in the slip plane, as expressed by the equation

$$\upsilon = A\tau^{m'} \tag{4}$$

where m' is a constant varying from about 1.5–40 depending on the material. A critical stress is required to initiate dislocations motion, and small increases in stress lead to a large increase in dislocation velocity. When indentation hardness is measured, local stress beneath the indenter will attain an extremely high value [18], so that the thermal activation effect on dislocation

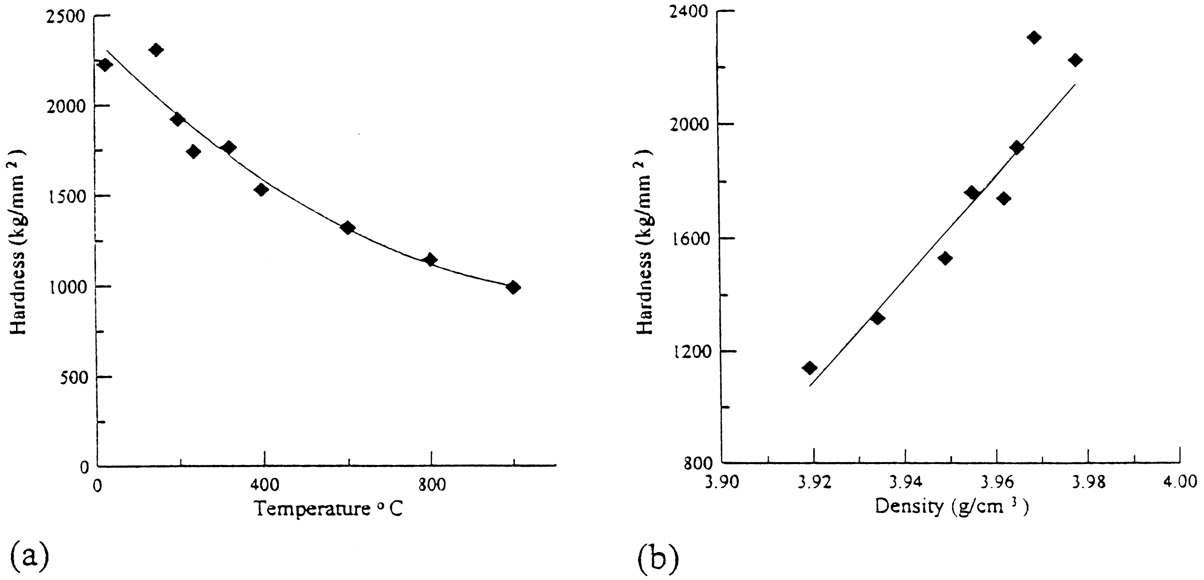

Fig. 1. The hot hardness dependence of Al_2O_3 on (a) temperature and (b) density (from Lankford [7]).

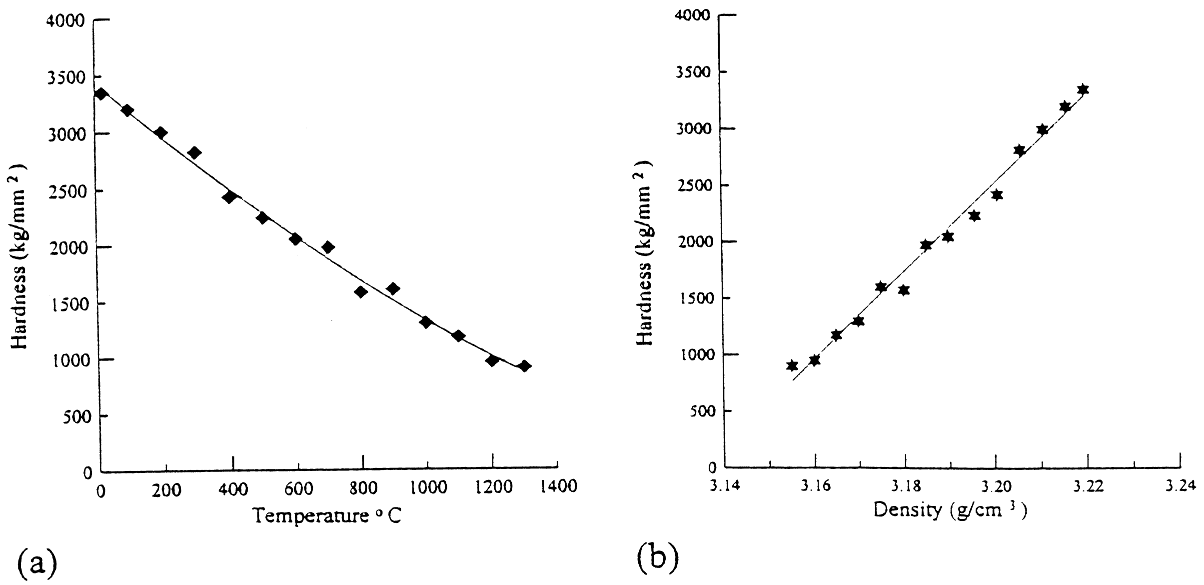

Fig. 2. The hot hardness dependence of SiC on (a) temperature and (b) density (from Loladze [10]).

velocity will not be comparable in such a case. Instead, the lattice spacing broadens with temperature increases, resulting in a reduced bonding strength, and the dislocation mobility may be enhanced by lowering the critical stress requirement. The interatomic potential energy in a structure is a function of interatomic spacing, as expressed by the equation

$$E = -a'/r^m + b'/r^n \tag{5}$$

where r is the interatomic distance and a', b', m and n are constants [19]. The progressive increase in dislocation motion achievable as core diffusion becomes easier at temperatures greater than 0.5 T_{mp} [20], and, the relation between creep and hardness measurement has been studied elsewhere [21]. The hot hardness data investigated in the present work were measured at a temperature lower than 0.5 T_{mp}, and with a short loading time no apparent creep would occur. Thus, at a low homologous temperature, the thermal activation of plastic deformation is not a dominant factor in softening while indentation plasticity exists.

The dependence of hardness on density (Figs. 1–4) shows that hardness may demonstrate an energy density

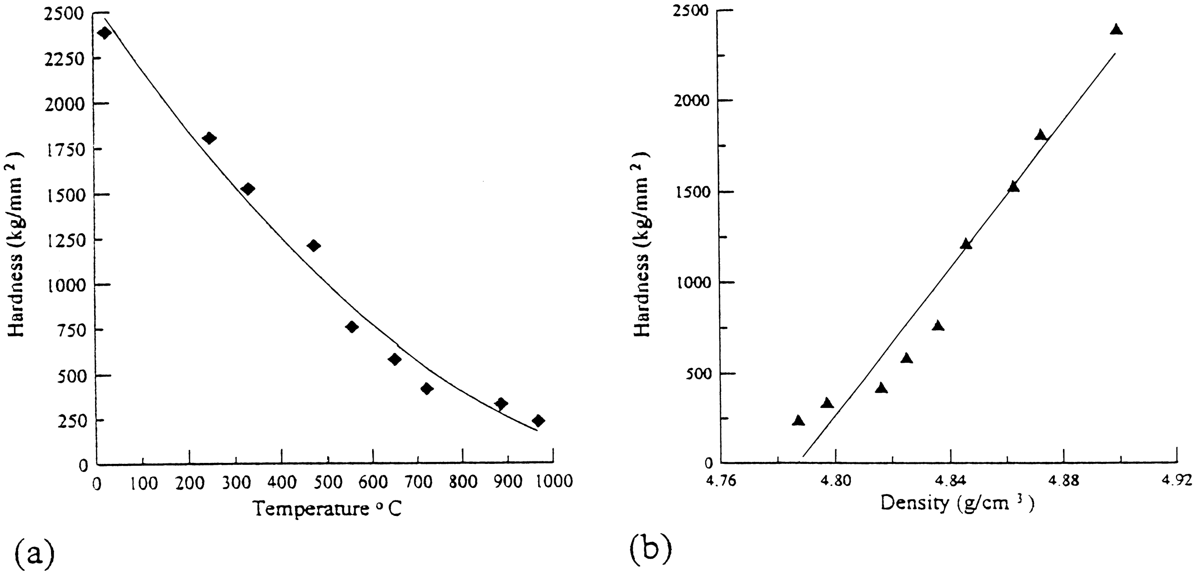

Fig. 3. The hot hardness dependence of TiC on (a) temperature and (b) density (from Loladze [10]).

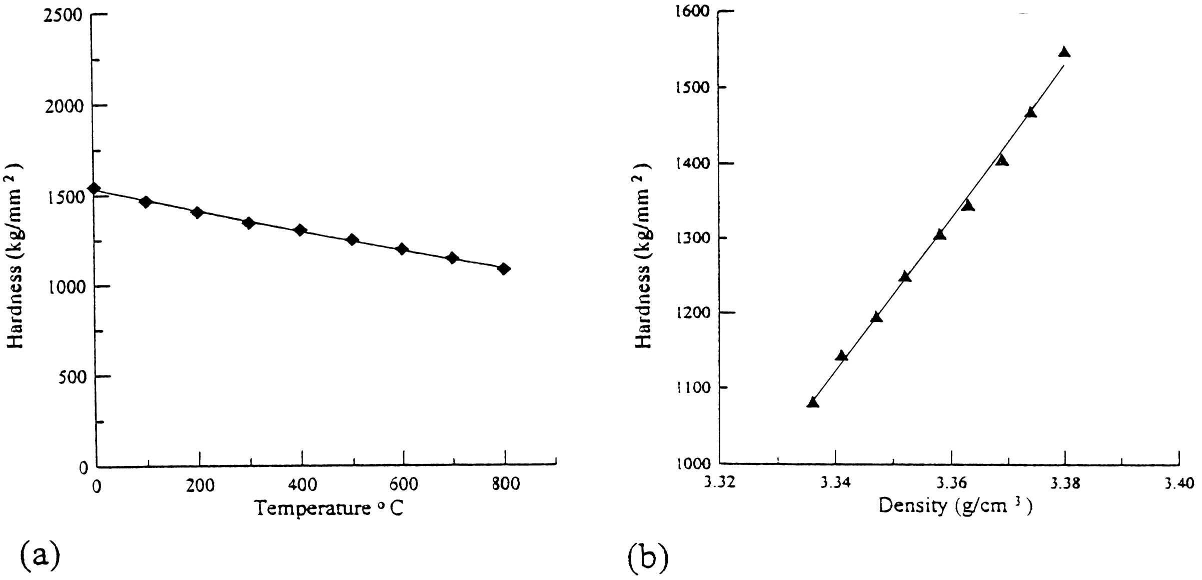

Fig. 4. The hot hardness dependence of mullite on (a) temperature and (b) density (from Hillig [9]).

characteristic. If Gilman's calculated function, $-2\Delta H_f/V_m$ is taken into account, for alumina, the ΔH_f [22] and V_m variation is 0.1 and 0.73%, respectively, when the temperature is raised from RT to 600°C. The energy density therefore is almost determined in this case by the density at various temperatures. As the temperature rises, the density decreases due to thermal expansion domination. A nearly linear relationship for the softening of ceramics thus emerges, and departures of the observed values from the function line may derive from such factors as measurement error, calculation simplification, and dislocation thermal activation, etc.

The constant a values listed in Table 1 represent the temperature sensitivity of hardness. Fig. 5 shows the relation between the constant a and CTE. Materials with larger CTE values have larger constant a values and hardness decrease more rapidly with increasing temperature. Those results confirm that the temperature dependence of hardness can be correlated with thermal expansion behavior of a material. For example, titanium carbide is harder than mullite at room temperature, with larger CTE and constant a value, but is softer at 800°C (see Figs. 3 and 4). Since TiC is often used as cutting tools in hard-metal machining, where very high

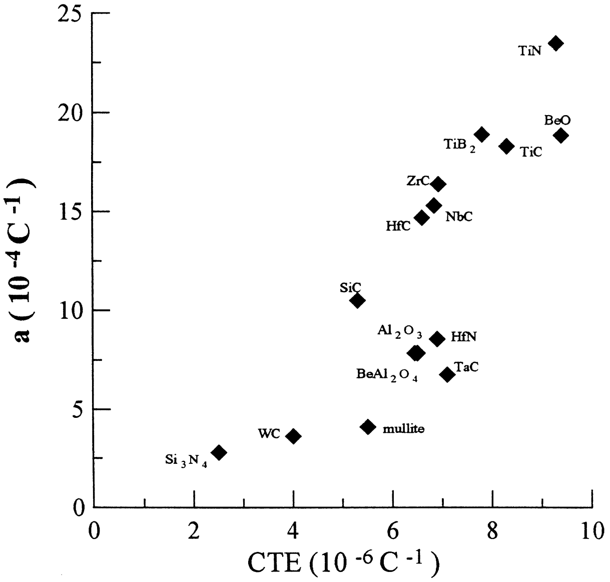

Fig. 5. The relationship between constant *a* and CTE of ceramics materials.

surface temperatures develop, the diminution in hardness is dramatic. The CTE value thus can be an important and convenient index for evaluating the high-temperature strength of ceramics, even though it does not serve absolutely to reflect the constant *a* value.

4. Conclusion

At low homologous temperature, in the absence of phase transformation, the hot hardness of ceramics is dependent on density. Ceramics with varying composition, bonding and structure exhibit similar behavior, implying that hardness may possess an apparent characteristic of energy density. Hardness degradation also correlates well with thermal expansion behavior, so material with larger thermal expansion coefficient will soften more rapidly than those with lower CTE values.

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