Intermetallics 19 (2011) 1275–1281

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Modeling hardness of polycrystalline materials and bulk metallic glasses

Xing-Qiu Chen*, Haiyang Niu, Dianzhong Li*, Yiyi Li

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Wenhua Road No. 72, Shenyang 110016, Liaoning, PR China

ARTICLE INFO

Article history:
Received 24 February 2011
Accepted 23 March 2011
Available online 2 June 2011

Keywords:
E. Mechanical properties, theory
B. Elastic properties

ABSTRACT

Though extensively studied, hardness, defined as the resistance of a material to deformation, still remains a challenging issue for a formal theoretical description due to its inherent mechanical complexity. The widely applied Teter's empirical correlation between hardness and shear modulus has been considered to be not always valid for a large variety of materials. The main reason is that shear modulus only responses to elastic deformation whereas the hardness links both elastic and permanent plastic properties. We found that the intrinsic correlation between hardness and elasticity of materials correctly predicts Vickers hardness for a wide variety of crystalline materials as well as bulk metallic glasses (BMGs). Our results suggest that, if a material is intrinsically brittle (such as BMGs that fail in the elastic regime), its Vickers hardness linearly correlates with the shear modulus ($H_v = 0.151G$). This correlation also provides a robust theoretical evidence on the famous empirical correlation observed by Teter in 1998. On the other hand, our results demonstrate that the hardness of polycrystalline materials can be correlated with the product of the squared Pugh's modulus ratio and the shear modulus ($H_v = 2(k^2G)^{0.585} - 3$ where $k = G/B$ is Pugh's modulus ratio). Our work combines those aspects that were previously argued strongly, and, most importantly, is capable to correctly predict the hardness of all hard compounds known included in several pervious models.

1. Introduction

Despite the great efforts, to understand the theory of hardness and to design new ultrahard materials are still very challenging for materials scientists [1–4]. During the past few years, several semi-empirical theoretical models [5–9] have been developed to estimate hardness of materials based on: (*i*) the bond length, charge density, and ionicity [5], (*ii*) the strength of the chemical bonds [6], (*iii*) the thermodynamical concept of energy density per chemical bonding [7], and (*iv*) the connection between the bond electron-holding energy and hardness through electronegativity [8], and (*v*) the temperature-dependent constraint theory for hardness of multicomponent bulk metallic glasses (BMGs) [9]. Experimentally, hardness is a highly complex property since the applied stress may be dependent on the crystallographic orientations, the loading forces and the size of the indenters. In addition, hardness is also characterized by the ability to resist to both elastic and irreversible plastic deformations and can be affected significantly by defects (i.e., dislocations) and grain sizes [10]. Therefore, hardness is not a quantity that can be easily determined in a well-defined absolute scale [1]. It has been often argued [13] that hardness measurements unavoidably suffer from an error of about 10%. All these aspects add huge complexity to a formal theoretical definition of hardness [5–9].

Within this context, to find a simple way to estimate hardness of real materials is highly desirable. Unlike hardness, the elastic properties of materials can be measured and calculated in a highly accurate manner. Therefore, it has been historically natural to seek a correlation between hardness and elasticity. The early linear correlation between the hardness and bulk modulus (B) for several covalent crystals (diamond, Si, Ge, GaSb, InSb) was successfully established by Gilman and Cohen since 1950s [10,11]. Nevertheless, successive studies demonstrated that an uniformed linear correlation between hardness and bulk modulus does not really hold for a wide variety of materials [1,12,13], as illustrated in Fig. 1(a). Subsequently, Teter [12] established a better linear correlation between hardness and shear modulus (G), as illustrated in Fig. 1(b). This correlation suggests that the shear modulus, the resistance to reversible deformation under shear strain, can correctly provide an assessment of hardness for some materials. However, this correlation is not always successful, as discussed in Refs. [5,13,14]. For instance, tungsten carbide (WC) has a very large bulk modulus (439 GPa) and shear modulus (282 GPa) but its hardness is only 30 GPa [15], clearly violating the Teter's linear correlation [see

* Corresponding authors.
E-mail addresses: xingqiu.chen@imr.ac.cn (X.-Q. Chen), dzli@imr.ac.cn (D. Li).

0966-9795/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.intermet.2011.03.026

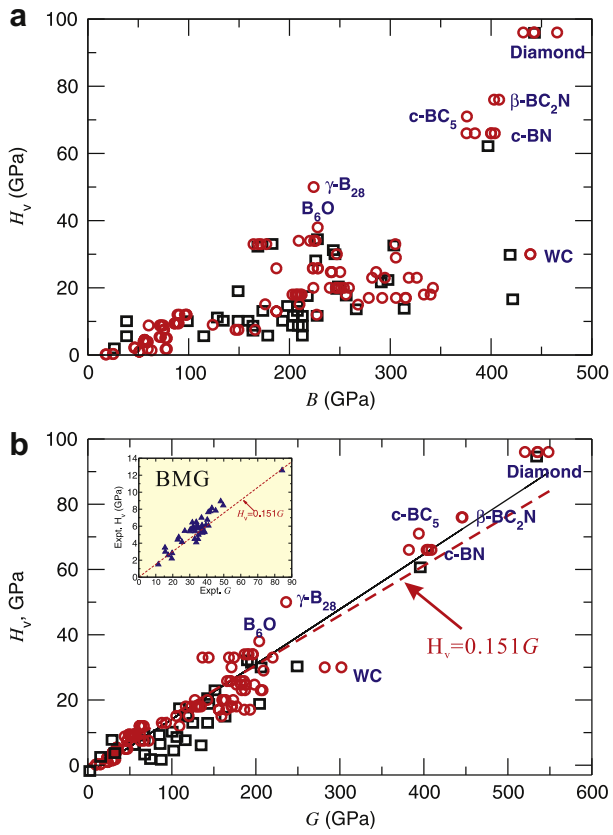

Fig. 1. Correlation of experimental Vickers hardness (H_v) with (a) bulk modulus (B) and with (b) shear modulus (G) for 39 compounds (Table 2). Inset of panel (b): H_v vs. G for 37 BMGs (see Table 1). The solid line denotes empirical Teter's fitting values, whereas dashed lines correspond to the value derived from Eq. (6). The black and hollow squares denote data taken from Refs. [1,12].

Fig. 1(b)] [5]. Although the link between hardness and elastic shear modulus can be arguable, it is certain to say that the Teter's correlation grasped the key.

In this manuscript, following the spirit of Teter's empirical correlation, we successfully established a theoretical model on the hardness of materials through the introduction of the classic Pugh modulus ratio of G/B proposed in 1954 [16]. We found that the intrinsic correlation between hardness and elasticity of materials correctly predicts Vickers hardness for a wide variety of crystalline materials as well as BMGs. Our results suggest that, if a material is intrinsically brittle (such as BMGs that fail in the elastic regime), its Vickers hardness linearly correlates with the shear modulus ($H_v = 0.151G$). This correlation also provides a robust theoretical evidence for the famous empirical correlation observed by Teter in 1998. On the other hand, our results demonstrate that the hardness of crystalline materials can be correlated with the product of the squared Pugh's modulus ratio and the shear modulus ($H_v = 2(k^2G)^{0.585} - 3$ where k is Pugh's modulus ratio). This formula provides the firm evidence that the hardness not only correlates with shear modulus as observed by Teter, but also with bulk modulus as observed by Gilman et al. Our work combines those aspects that were previously argued strongly, and, most importantly, is capable to correctly predict the hardness of all compounds included in Teter's [12], Gilman's [4,10], Gao et al.'s [5] and Šimůnek and Vackář's [6] sets. Also, our model clearly demonstrates that the hardness of bulk metallic glasses is intrinsically based on the same fundamental theory as the crystalline materials. We believe that our relation represents a step forward for the understanding and predictability of hardness.

2. Model and results

According to Vicker [10], the hardness of H_v is the ratio between the load force applied to the indenter, F, and the indentation surface area:

$$H_v = \frac{2F\sin(\theta/2)}{d^2}, \tag{1}$$

where d and θ are the mean indentation diagonal and angle between opposite faces of the diamond squared pyramid indenter, respectively (Fig. 2). In order to derive our model, we first assume that (i) the diamond squared pyramid indenter can be divided into four triangular based pyramid indenters and that (ii) the Vickers hardness is measured within the elastic scale. Then, for each triangular based pyramid, one can define the shear modulus G as,

$$G = \frac{F}{4A\tan(\alpha)} \tag{2}$$

which specifies the ratio between shear stress and the shear strain. In terms of our model the exact shear area A on which the shear force (F) acts is unknown. But, the deformation area A^* [$A^* = 1/8d^2\tan(\alpha)$] delimited by the klO′ triangle is well defined by the indentation geometry. Therefore, we can express the exact shear area (A) as:

$$A = cA^* = \frac{c}{8}d^2\tan(\alpha), \tag{3}$$

where c is the proportional coefficient. It is clear that under elastic shear deformation the deformation area (A^*) will be extremely small. However, upon real hardness measurements the deformation area (A^*) should be large enough so that the coefficient c can be safely neglected and $A \approx A^*$. Under this assumption, equation (2) can be revised as following,

$$G = \frac{2F}{d^2\tan^2(\alpha)} \tag{4}$$

Combining equations (1) and (4), the Vickers hardness reads

$$H_v = G\tan^2(\alpha)\sin(\theta/2) = 0.92G\tan^2(\alpha), \tag{5}$$

where the term $\sin(\theta/2)$ is intrinsically determined by the indenter itself, which can be considered as a constant (originated from the Vickers hardness, see equation (1)). For the diamond squared pyramid indenter with $\theta = 136°$, $\sin(\theta/2)$ is equal to 0.92 for Vickers hardness measurement. In an ideal form of indentation, $\tan(\alpha) = 0.404$ because of $\alpha = (\pi - \theta)/2.0$ (*c.f.*, Fig. 2). Therefore, equation (5) can be simplified as,

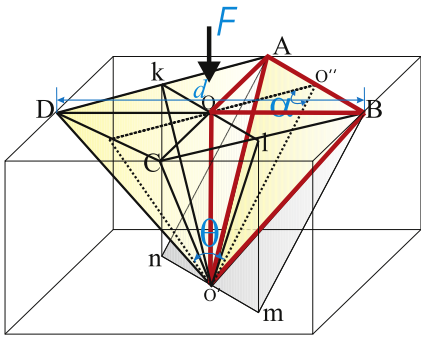

Fig. 2. Illustration of indentation in terms of the squared diamond pyramid indenter. The red framework highlights one of four triangular based pyramid indenters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)