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Review

Mechanical and tribological properties of ceramic/metal composites: A review of phenomena spanning from the nanometer to the micrometer length scale

T. Rodriguez-Suarez a,*, J.F. Bartolomé b, J.S. Moya b

^a Centro de Investigación en Nanomateriales y Nanotecnología (CINN), Consejo Superior de Investigaciones Científicas (CSIC), Universidad de Oviedo (UO),
Principado de Asturias (PA), Parque Tecnológico de Asturias, 33428 Llanera, Asturias, Spain

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Abstract

In the present work, the recent advances and promising potential applications of new developed ceramic (alumina, zirconia, spinel)/metal (Ni, Nb, W) micro/nanocomposites are discussed. We review the exotic properties of metal particles embedded into ceramic matrices and the effect of the percolation law, the nature of the interfaces and the size effect (micro/nano). This article discusses the material's mechanical and tribological properties, such as hardness, wear resistance and toughness.

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1. Introduction

With the evolution of technologies, the design and development of new materials is mandatory to satisfy the required

^b Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), C/Sor Juana Inés de la Cruz 3, 28049, Madrid, Spain

^{*} Corresponding author. Tel.: +34 985733644; fax: +34 985265574. E-mail address: t.rodriguez@cinn.es (T. Rodriguez-Suarez).

specifications. The great variety of applications is such that even all imaginable material combinations can fulfil a specific purpose. In this scenario, ceramic/metal composites are possible candidates to meet the expectations that are not achievable by monolithic materials. The most obvious advantage of ceramic/metal composites is that they can favourably integrate the often dissimilar properties of ceramic and metal components in one single material. As a consequence of the large variety of multiple combinations this field is very innovative, since it provides the opportunity to create an almost unlimited set of new materials with a large spectrum of known and as yet unknown properties.

Although the increasing interest regarding ceramic/metal composites is developed during the late 1980s and early 1990s, two decades later a great effort is still devoted to design new custom-made materials to meet the expectations for top end industrial or even biomedical applications.

By the inclusion of metallic micro- or nano-particles into a ceramic matrix, their properties can be dramatically changed, yielding mechanically or tribologically improved materials. Properties such as the toughness, the flexural strength, the hardness and also the wear resistance can be improved, achieved not only by the use of the most advanced sintering techniques, as spark plasma sintering (SPS), but also by conventional sintering techniques.

Physical properties do not scale with particle size as it is the case of the mechanical properties. Superplasticity has been observed in nanostructured monolithic materials and also stiffness or supermodule and hardening phenomena, better known as Hall–Petch effect. ^{1–4}

Considering the latter effect, the threshold stress (and indirectly the hardness) increases for small particle sizes. In the particular case of metals, hardening enhancements by a factor of 10 in Cu nanoparticles^{5,6} and by factors between 3 and 5 for hard covalent materials coatings (TiN, SiC, etc.)⁴ have been reported.

On the other hand, the increase in the elastic constants indirectly induces a hardness increase to the nanoparticles. It is known that there is almost a linear correlation between the hardness and shear module (*G*) for non-plastic materials. In this way, hardest materials (diamond, cBN, WC, etc.) are also the stiffest. If the same rule is applied to the case of metal nanoparticles, it suggests that an increase in the elastic modulus would directly and positively affect the hardness since the nanoparticles would not be affected by a plastic deformation due to the lack of dislocations.

It was stated by Teter⁷ that when plotting hardness (H_v) versus shear modulus (G) for materials where no plastic deformation occurs, such as ceramics, data could be fitted reasonably well by a straight line (increasing hardness with G module). On the other hand, in the case of metals where plastic deformation in bulk materials takes place, this relationship does not exist and materials are randomly distributed in this plot. For nanometals, where dislocations are not present or are blocked, it is expected that the data follows the same trend as the ceramics.⁸ Hence, the higher G, the higher hardness improvement could be achieved. Therefore, a higher G value also implies a higher hardness.

Recently, another method to consider the design of ultrahard materials has been published by Veprek et al. In this work authors report that intrinsically super- $(H \approx 40-70 \, \text{GPa})$ and ultra-hard $(H \geq 70 \, \text{GPa})$ TmN type materials (Tm referring to a transition metal) attain high hardness through their nanostructure. These authors report that materials can reach hardnesses significantly larger than for diamond when they are optimally prepared and defect free. Such superhard nanocomposites are already available on an industrial scale as protective coatings on tools for machining, such as for drilling, milling, turning, forming and stamping.

The structure of ceramic/metal nanocomposites has not been as thoroughly studied as the ceramic/ceramic nanocomposites, where specially covalent systems formed by an amorphous matrix with hard crystalline nanoparticles embedded^{4,10} have attracted scientific interest. However, during the last years, the dispersion of a second metallic phase (Mo, Ag, Ni, W, Cu, Co, etc.) as nanoparticles (<100 nm) in a ceramic matrix (Al₂O₃, ZrO₂, etc.) has been widely studied and it has been stated that the mechanical properties (hardness and flexural strength) can be notably improved with respect to the monolithic ceramics. ^{11–17} On the other hand, it is well known that metals in the nanometric range show less ductility than the same materials with bigger grain sizes. ¹⁸

One of the most promising applications for these hardness improved nanostructured materials is as cutting and/or machining tools. Many efforts are being devoted for designing superhard materials (with hardness higher than 25 GPa). Diamond is the hardest naturally occurring material known and is irreplaceable in roughing tools, drills, cutting tools for cements, polishing stones and general purpose machining tools. However, the main drawback is the reaction with Fe, Ti and Si and thus cannot be used, for instance, for machining steels or cast iron. This limitation has promoted the synthesis of other alternative superhard materials such as carbides, nitrides and borides. All these materials have some common features, i.e. they contain directional covalent bonds and possess a very high shear modulus. 19 However, the synthesis of these intrinsically hard materials requires extreme conditions, such as high temperatures and pressures.²⁰ Thus, efforts have been devoted to develop superhard materials based on the peculiar properties of nanoparticles.

Ceramic/metal microcoposites can be, generally speaking, considered as structural materials. However, ductile metals acting as isolated second phases, which are more than scientific curiosities, are not yet fully established as engineering materials.²¹ One of the most effective methods to increase fracture toughness in monolithic ceramics is by incorporating ductile metal particles reinforcements. The reinforcement interacts with the pre-existing and/or service induced cracks to slow down their propagation. Previous experimental studies ^{22–25} have shown that the primary mechanism responsible for the enhanced toughness of ceramic/metal composites is the elasto-plastic bridging across the crack path, operated by intact ligaments. Ceramic/metal composites with adherent ductile phases exhibit generally stable crack-growth resistance behaviour (Rcurve). 22,26-29 The bridging ligaments exert closure stresses which reduce the stress intensity at the crack tip and offer

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