

A quantitative in vitro method to predict the adhesion lifetime of diamond-like carbon thin films on biomedical implants

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Abstract

A quantitative method using Rockwell C indentation was developed to study the adhesion of diamond-like carbon (DLC) protective coatings to the CoCrMo biomedical implant alloy when immersed in phosphate-buffered saline (PBS) solution at 37 °C. Two kinds of coatings with thicknesses ranging from 0.5 up to 16 microns were investigated, namely DLC and DLC/Si-DLC, where Si-DLC denotes a 90 nm thick DLC interlayer containing Si. The time-dependent delamination of the coating around the indentation was quantified by means of optical investigations of the advancing crack front and calculations of the induced stress using the finite element method (FEM). The cause of delamination for both types of coatings was revealed to be stress-corrosion cracking (SCC) of the interface material. For the DLC coating a typical SCC behavior was observed, including a threshold region (60 J m^{-2}) and a “stage 1” crack propagation with a crack-growth exponent of 3.0, comparable to that found for ductile metals. The DLC/Si-DLC coating exhibits an SCC process with a crack-growth exponent of 3.3 and a threshold region at 470 J m^{-2} , indicating an adhesion in PBS at 37 °C that is about eight times better than that of the DLC coating. The SCC curves were fitted to the reaction controlled model typically used to explain the crack propagation in bulk soda lime glass. As this model falls short of accurately describing all the SCC curves, limitations of its application to the interface between a brittle coating and a ductile substrate are discussed.

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1. Introduction

Coating delamination is one of the principal and, up to now, unpredictable causes of failure in articulating biomedical implants coated with diamond-like carbon (DLC) [1]. The speed of delamination largely influences the lifetime of the coated implant; it can range from millimeters per day down to micrometers per year. While rapid delamination of the order of hundreds of micrometers per day can easily be observed, very slow delaminations of the order of a few micrometers per year are not so easy to detect. However, delaminating microscopic spots growing at just

a few tenths of a micrometer per year can determine the failure of the coated implant after several years. Therefore, in order to estimate the in vivo lifetime of a coated implant it is crucial for the industry to use a quick and reliable in vitro method to determine the speed of coating delamination. Although many qualitative studies of the mechanisms involved in DLC-coated implant failure exist [2–4], to our knowledge no quantitative method is available to assess the lifetime of the coated implant.

The Rockwell indentation test is a well-established metallurgical tool used to determine the hardness of materials [5]. More recently, this method has also been used in the coating industry to qualitatively assess the adhesion of brittle films to metallic surfaces [6]. The mechanics of the Rockwell indentation test have been numerically analyzed

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by Drory and Hutchinson [7], who proposed a method to determine the fracture toughness of an interface. This model considers that delamination around the Rockwell indentation stops as soon as the layer strain energy responsible for film delamination equals the effective adhesion energy. Although these authors point out that the composition of the interface may play a role in obtaining reproducible interface toughness data, they do not consider the implications of the interface chemical state for film delamination. For example, they consider a peculiarity of thin films in compression – that the interface can be tougher than the film and still be the fracture path – but overlook that the fracture toughness of an interface can be significantly lowered in corrosive media [8]. Thus, in corrosive media, and to some extent even in air, the delamination could still continue far away from the indentation in regions where the only contribution to the elastic strain energy is the residual stress of the coating.

Basically, due to the strong plastic deformation generated by indentation, the shear stresses at the film–substrate interface raise the elastic energy of the film above the adhesion energy of the film and interface cracks are formed. Consequently, the film/substrate system will fail locally due to the loading of the interface above the critical limit, and this is known in fracture mechanics as catastrophic or critical failure. By adhesion energy, one means the macroscopic work of fracture per unit area necessary to separate the interface of interest. This is usually quantified by the critical strain energy release rate, G_c , which is a function of both materials properties (e.g. interface chemistry, elastic–plastic behavior) and mechanical parameters (e.g. loading mode).

The influence of residual stress on debonding behavior of DLC films on several metallic substrates (e.g. Ti, Al, 316 stainless steel and mild steel) with interfaces prepared in various ways was analyzed by Peng and Clyne [9,10]. These authors determined G_c by depositing films of various thickness and observing whether or not they had debonded during in situ deposition, or when the chamber was opened after deposition and cooling. It was found out that for Ti and both types of steel the toughness of the interface is low ($G_c \sim 7 \text{ J m}^{-2}$), whereas for Al the adhesion is much better ($G_c > 100 \text{ J m}^{-2}$). The adhesion on Al was further increased by Ar ion bombardment precleaning of the substrate ($G_c \geq 350 \text{ J m}^{-2}$). Although these authors mentioned that DLC may buckle when exposed to air for prolonged periods, they do not consider that the G_c of DLC-coated metal systems can be reduced in a relatively short time as a result of corrosive processes triggered by the moist air environment. For instance, we observed that, on storing the coated samples in vacuum instead of air, the delamination stopped almost completely [11].

The environmental species (e.g. liquid, air, etc.) can diffuse to the interface through the cracks induced by indentation or film defects (e.g. pinholes), and interact with the chemical bonds at the crack tip, reducing thus the toughness of the interface below the elastic energy stored in the

thin film. Consequently, film/substrate structures can fail by progressive film delamination at stresses far below those required for catastrophic failure, $G \ll G_c$. This is known as subcritical failure. Such delamination can be associated with environmentally assisted crack growth or stress-corrosion cracking (SCC) [12,13].

While the term “stress-corrosion cracking” is typically used to describe failures in metallic alloys, other classes of materials, such as ceramics, glasses and polymers, also exhibit delayed failure by environmentally induced crack propagation [12,13]. Although the SCC in bulk carbides has been only scantily investigated, it is generally accepted that the presence of carbide precipitates at the grain boundaries of a large variety of steels and metallic alloys (also containing Co, Cr and Mo) creates metal-depleted zones that are prone to intergranular, and sometimes even transgranular, corrosion [12]. Since, in the case of DLC-coated metallic biomedical implants, an $\sim 2\text{--}10 \text{ nm}$ thick reactive layer consisting of metallic (Co, Cr and Mo) carbide bonds is formed at the interface between the DLC layer and the metallic substrate [1], it cannot be excluded that an SCC mechanism in this layer occurs in vivo.

In brittle materials such as ceramics and glasses, and to some extent also in metal alloys, the environmental mechanism leading to crack propagation is described by a three-stage reaction involving molecules of the reactive species and the strained chemical bonds at the crack tip [12,13]. Thus, diagrams of the typical crack-propagation rate (i.e. delamination speed, v) as a function of the stress intensity (K) at the crack tip, or strain energy release rate (G), have a sigmoidal shape like the one presented in Fig. 1, in which the changes in slope indicate a change in the rate-limiting

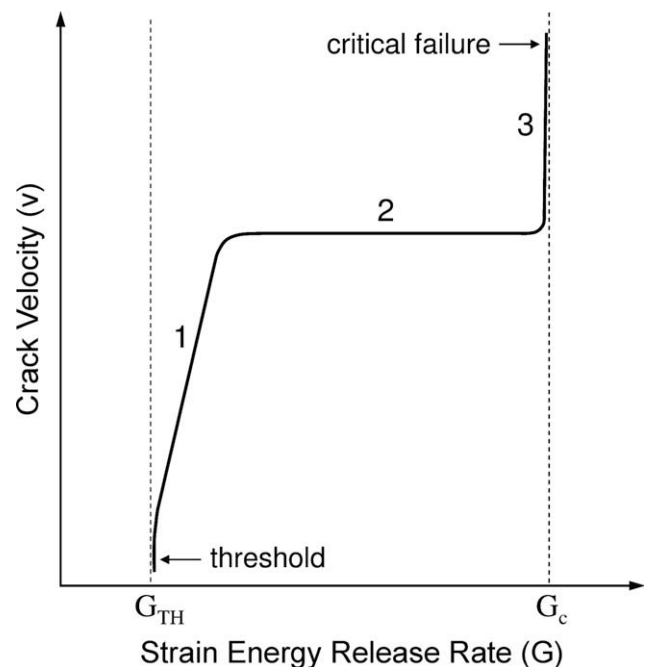


Fig. 1. Typical SCC curve for bulk ceramics, glasses, as well as metals, showing the three stages of crack propagation.

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