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Friction and adhesion of single spray-dried granules containing a hygroscopic polymeric binder

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Abstract

The atomic force microscope has been used to study the friction and adhesion of single spray-dried granules containing a mixture of fine tungsten carbide and cobalt powders and various amounts of a polymeric binder, polyethylene glycol (PEG). The pull-off and friction forces between two single granules (representing intergranular friction) and between a granule and a hard metal substrate (representing die–wall friction) have been determined as a function of relative humidity. It was found that the granule–wall friction increased with binder content and relative humidity. The small friction force at the lowest addition of PEG was related to a small contact area due to the high surface roughness of the granules. The substantial increase in the friction coefficient at PEG-addition >1 wt.% was related to the plasticity of the binder-rich granule surface where an increase in binder content or relative humidity increases the deformability. The granule–granule friction and adhesion was independent of the relative humidity and substantially lower than the granule–wall friction at all PEG contents, which has important implications for the handling of granular matter.

Keywords: Friction; Granule; PEG; Hard metal; Pressing; AFM

1. Introduction

Dry pressing and cold isostatic pressing are probably the most important forming techniques for industrial production of ceramic and hard metal materials [1,2]. Green bodies are formed by pressing free flowing granules in a die. The granules are formed from a suspension of a fine powder and a polymeric binder using a granulation technique, e.g. spray-drying or freeze granulation [3,4]. It is well known that the quality of the pressed body strongly depends on the properties of the granules [5–13]. If the granules are not completely broken-down during pressing, the remnant structure may induce large defects during sintering. Hence, the granules should not be too hard. However, soft granules may cause problems with handling and mould filling since granule fracture and deformation will have a negative effect on flowability. The deformation behaviour of the granules is strongly affected by the physical properties of the polymeric binder. Several studies have shown that densification of granulated powders is enhanced when the glass transition temperature, T_g, of the binder is lowered below the pressing temperature [8,11,13]. The binder deforms plastically at temperatures above the T_g and the intergranular pores are thus more easily eliminated. Binders commonly used for pressing of fine ceramic and hard metal powders are poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG). The T_g for pure PVA is normally above room temperature. However, PVA can be plasticised, i.e. T_g can be reduced, by the addition of low molecular weight polymers e.g. poly(ethylene glycol) (PEG). PVA is also plasticised by the absorption of water, which means that the pressing performance can vary drastically with relative humidity [9]. In contrast, PEG has a T_g below 0 °C and thus deforms viscoelastically at room temperature. Hence, sufficient granule

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deformation may be achieved without the addition of a plasticiser if PEG is used as a binder [12,13]. However, the hygroscopic nature of PEG and the reduction in hardness with water uptake also makes this binder sensitive to changes in relative humidity [13]. The water-soluble polymeric binder can migrate to the granule surface during spray-drying, which enhances the importance of the binder properties controlling the friction between granules [14,15]. There have been some attempts to relate the frictional behaviour of granular assemblies to the filling, rearrangement and pressing properties [5–10]. Briscoe and Rough found that a poor rearrangement of the granules at the early stages of pressing, which was related to a large die–wall friction, induces stresses in the compacted part that may lead to cracking upon ejection [6]. Recent work by Balasubramanian et al. showed that a reduction in the intergranular porosity could be achieved by the addition of an internal lubricant that results in an enhanced granule rearrangement [5].

Despite the importance of friction and adhesion in controlling the rearrangement of the undeformed granules at low applied pressures, there is a lack of fundamental studies on the level of the single granule. Microscopic friction and adhesion measurements were greatly facilitated by the introduction of Friction Force Microscopy (FFM) by Mate et al. [16]. They used the atomic force microscope (AFM) for friction force measurements between a tungsten tip and a graphite surface. Since then the progress in detector and cantilever calibration techniques has enabled quantitative friction measurements on a nanoscopic length scale. Implementing the *colloidal probe* technique [17], where a spherical particle of a size ranging from a few micrometers up to the order of 50 μm of an arbitrary material is attached to the cantilever, has facilitated the investigation of frictional properties of a wide range of materials [18–25]. Jones showed in a recent study that FFM measurements can be related to bulk flow and cohesion measurements, at low consolidation stresses, for a range of model particles and cohesive granular materials [22]. Meurk et al. showed in one of the few previous FFM studies on granules that the relative humidity has a strong effect on the adhesion and the friction coefficient [24].

In this study, the FFM technique was used to investigate the adhesional and frictional response of spray-dried WC–Co granules containing various amounts of PEG as a binder. Both the granule–wall and granule–granule friction have been measured. The single granule FFM measurements clearly illustrate the importance of humidity and binder concentration on the granule–wall friction and adhesion. It was shown that the intergranular friction coefficient was lower than the external friction coefficient (between a granule and a flat surface). The implications of the single granule data on the filling, rearrangement and pressing properties of granule assemblies were discussed.

2. Experimental

2.1. Materials

The granulated powder, provided by CERMeP (Grenoble, France), was produced from an aqueous powder suspension of 12 vol.% solids loading using a laboratory spray-drier (Anhydro, Denmark) with a capacity of evaporating 7.5 kg of water per hour. The hard metal powder is a mixture of 89.5% fine grain WC (grain size 0.5–1 μm after sintering), 10% Co, and 0.5% Cr_3C_2 by weight. The binder was polyethylene glycol, PEG, with a molecular weight MW=3400 (BASF, Ludwigshafen, Germany). Four different concentrations of PEG: 0.5, 1, 2, and 3 wt.% (weight % of the solids content of the suspension) were added to the powder suspension prior to spray-drying.

We have used a polished hard metal pressing tool punch provided by AB Sandvik Coromant (Stockholm, Sweden) as the substrate for the granule–wall measurements. The material consisted of 94.3 wt.% WC (grain size of 1 μm), 5 wt.% Co, and 0.7 wt.% Cr_3C_2. The RMS surface roughness of the polished surface is 3.4 nm as evaluated from a 10×10 μm AFM topographic image. Substrates for the granule–granule measurements were prepared by gluing WC–Co granules onto a flat metal disc. An example of a substrate with granules of a typical size around 150 μm is shown in Fig. 1.

The surface roughness of the spray-dried granules containing various amounts of PEG binder was measured using a non-contact profilometer (ZygoLOT New View 5000, ZygoLOT GmbH, Germany). The interference pattern of two light beams reflected from the granule and a reference surface, respectively, is used to determine the topography and surface roughness parameters [26]. The surface roughness is determined from the average of at least 35 granules.

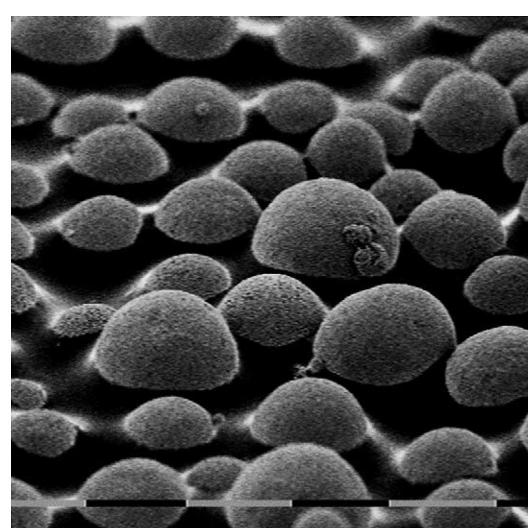

Fig. 1. SEM image of a granule substrate used for granule–granule friction measurements. The length of the size bar is 100 μm.