USE OF CERAMICS FOR GEOTHERMAL AND MINING APPLICATIONS

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Abstract

Metals have historically been used in mining since they offer an excellent combination of hardness, toughness and cost and can be fabricated to form a variety of shapes. However, for many applications the metals used today have limited performance in the environments in which they are needed. This is particularly true for geothermal environments where the brines are highly siliceous causing corrosion and accelerated wear of many components. Geothermal sources are increasingly being explored for their high thermal value as well as possible sources for future minerals.

While advanced ceramics have historically been expensive to produce in comparison with metals, they offer significantly greater corrosion resistance and hardness and can improve the overall performance when used in selected "problem" areas. One of the major drawbacks in the use of ceramics in high impact areas has been their brittle nature and propensity to fracture and spall (fail) when loaded. Recent advances in the fabrication of ceramics have combined hard (strong) ceramics with more ductile ceramics in a architecturally designed microstructure, thus allowing ceramics to perform well in these high impact regions.

Additionally, ceramics are significantly more inert to corrosion from either alkaline or acidic environments and can typically be used for significantly longer periods in these environments than their metallic counterparts.

Introduction

There are a variety of wear mechanisms that affect all materials used in mechanical applications. The wear is generally not limited to one type but a combination of different mechanisms. The properties of most metals cause them to wear through abrasion and erosion. The wear of metals against one another can be influenced by the hardness of the bearing metal, the temperature of operation and the presence of contaminants and even caustic environments. For ceramic bearings the wear mechanisms can be the same or they can also be caused by sliding, fretting or spallation.

Ceramic materials for bearings, seals, wear plates and drilling equipment are advantageous since they don't normally suffer from the high wear rate seen for metals where the surface is soft enough to abrade or be eroded away by contact with rough materials or reactive environments. Current applications for ceramic seals include high temperatures, caustic environments, and extreme wear applications.

Due to high melting points and hardness ceramics are extremely tolerant of harsh environments. For these environments ceramic materials such as silicon nitride and silicon carbide have already shown themselves to be excellent materials. Depending on the level of abrasive wear aluminum oxide has also proven to be an extremely durable material.

Corrosion Resistance of Ceramics

Certain types of ceramics demonstrate different types of wear based on the conditions they are surrounded by. Differences between dry and moist conditions are striking since, for silicon nitride ceramics, if the condition are moist a linear wear the increases with time is seen. The same formulation of ceramic exposed to dry wear conditions starts as a linearly increasing wear and shifts to much more rapid decomposition with fretting and exponential decomposition of the contact surface.

An additional consideration for the wear of ceramics such as silicon carbide (SiC) is the pH and temperature range of the systems (water solutions) where they are working [1]. For exposure to high pHs the wear on SiC is described as parabolic as shown in Figure 1. The wear of the same material under low pH conditions is linear as would be preferred for mechanical seals, bearing and pump applications. Figure 1 also illustrates the accelerated corrosion as the oxygen partial pressure is increased. It is suggested that the responsible mechanism is formation of a scale of silicon dioxide (SiO_2) as would be seem during dry wear but no degradation of the SiO_2 and protection over the long term as a result.

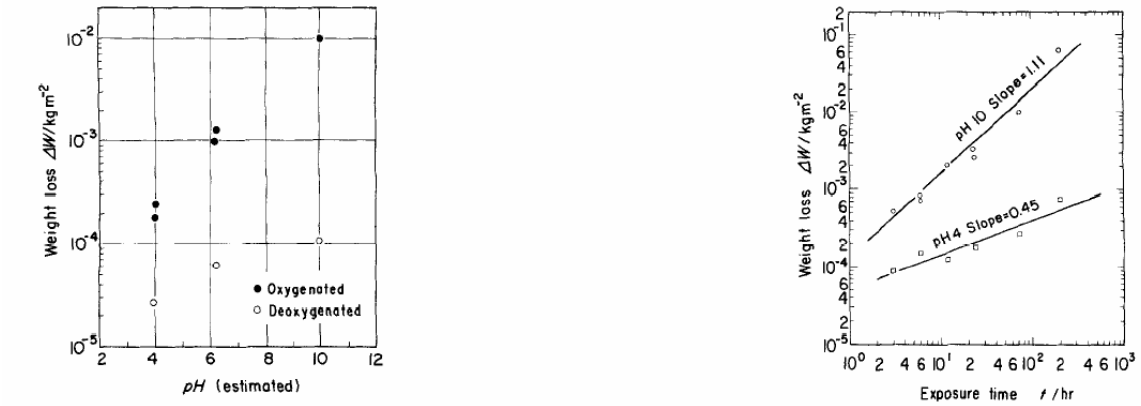

Figure 1. Weight loss for SiC after 72 hours in different pH solutions at 290°C (right) and in an oxygenated solution (left)[1].

Wear mechanisms in ceramics are analogous from one material to another (e.g. silicon carbide, polycrystalline alumina, alumina/alumino-titanate composites, silicon carbide/titanium diboride composites, and silicon nitride) and for sliding wear generally follow the mechanisms of mild plastic-controlled wear (polishing) then severe fracture-controlled wear (grain pullout) [2]. The influences in this type of wear are grain size, grain boundary toughness, internal residual stresses, macroscopic residual stresses and hardness)[3]. Through intentional manipulation of these characteristics, were possible, the wear properties of ceramics may be enhanced for the intended environment.

Other avenues for enhancement of the performance of ceramic materials are the inclusion of graded structures such as silicon nitride/silicon carbide for contact damage resistant ceramics, fiber reinforcements as in silicon nitride/carbon fiber composites for dry sliding applications, and glass infiltration of alumina structures for wear resistance in wet sliding applications [3],[4],[5].

While the various mechanisms involved vary, the combined properties of the systems mentioned have superior performance to those of the ceramic alone.

The reasons for the improved performance of these and other systems are due to the ability to improve thermal conductivity, reduce the coefficient of thermal expansion, improve plastic deformation at high temperatures, modify the grain boundaries to improve thermal resistance, and enhance the surface film formation during wear [6].

Drilling and Grinding Requirements

The removal of ore from the ground is achieved by employing drilling, scraping and cutting operations in which the ground breaking device is exposed to a combination of high stress grinding, abrasion and impact often under conditions of elevated temperature and pressure. In geothermal environments not only is the rock hard and at elevated temperatures, but often the liquor contained in the geothermal source is corrosive and leads to accelerated aging of the components. The material properties desired for grinding or drilling tools are a combination of strength and high hardness to overcome the high strain abrasion from the constant movement against the rock under high load, and very high toughness to survive the impact of the material as it is loaded and unloaded. In the past, high toughness cemented tungsten carbide have been used to provide the combination of high hardness (brittle, tungsten carbide (WC)) with high toughness (a more ductile cobalt (Co) cementing phase). For drilling and cutting operations hardness is synonymous with wear resistance, particularly for abrasive wear applications - the higher the hardness the higher the wear resistance.

In an effort to improve the damage resistance of wear materials, fibrous monolith (FM) materials have been developed in which the microstructure is organized into repeating regions of hard, wear resistant materials surrounded by a layer of more ductile, damage tolerant material [7]. In this way low wear rates can be achieved from having a high hardness material integrated into a damage tolerant microstructure in which cracks are interrupted locally, thereby avoiding the chipping and failure associated with normal tool failure [8].

The optimal wear material exhibits a combination of exceptional hardness together with exceptional toughness, usually a characteristic property brought about by ductility. These two characteristics are however mutually exclusive, and hard wear resistant materials are typically brittle and offer little resistance to the propagation of cracks. Similarly materials that exhibit toughness do so since they offer a resistance to the propagation of cracks either by a tortuous crack path, ductile phases which tend to blunt cracks or the phase transformation of one of the phases and an expansion in volume which tends to resist crack propagation. At the rock/tool-interface, rubbing and impact loads give rise to abrasion of both the tool and the rock, often cause uncontrolled chipping and significantly reduces the useful life of the wear part. Fibrous Monoliths materials combine cells of predominantly “hard” materials (e.g. WC) surrounded by a cell wall of more ductile materials with a higher Co content in a regular and predictable pattern. This architecture significantly improves the damage tolerance of the surface limiting the surface initiated cracks to the scale of the cell (between approximately 100μm to 500μm). Figure 2 shows a typical fibrous monolith structure in which the primary extruded cell can be seen as the core of a

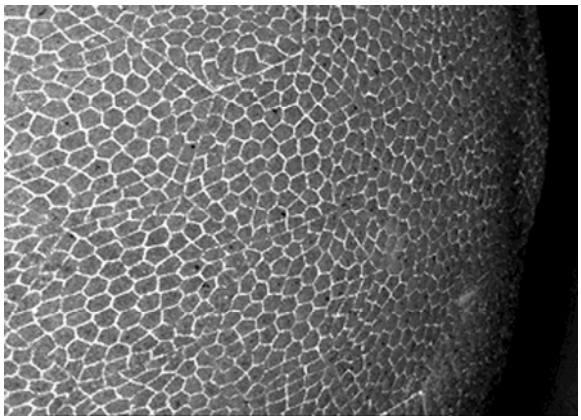

Figure 2. Fibrous monolith honeycomb architecture on surface of button tool.

honeycomb clad with a second material usually ductile in nature. The FM materials have been produced from a wide variety of materials and evaluated for drilling and cutting applications, as well as for metal extrusion dies and other wear components for use in extreme environments.

A series of button inserts were fabricated as shown in Figure 3 and evaluated for tri-cone roller bits (Figure 3). In these inserts the core material was hard with 3% to 6% by wt WC and Co and the tougher cell wall material, ranged from 16% to 25% Co by wt. respectively, and accounted for 17.5% by volume of the total volume. There are many variables such as the core and shell material composition, cell wall thickness and volume fraction etc., which can be altered in this arrangement, and there are presently no approaches other than by fabricating and testing the parts to evaluate their performance.



Figure 3. FM inserts and a tri-cone roller bit in which they were tested.

Hierarchical, microstructural modeling of this architecture is presently underway using a program called DENDRO [9],[10],[11] to optimization the material selection and FM design selected.

Past Experience with Ceramic Wear Parts

Using the fibrous monolith technology and comparing this with monolithic ceramics, a number of components have been fabricated and evaluated for a range of applications. The materials used have included silicon carbide, tungsten carbide, silicon nitride, alumina and a number of composite systems formed with fibrous monolith technology.

Tunnel boring inserts

Tungsten carbide FM inserts were fabricated and tested in a tunnel boring machine in Australia as shown in Figure 4. These tests were completed and the ceramics performed well. The overall data is inconclusive due to insufficient data from a which a comparison could be drawn. Catastrophic failure of the tunnel boring insert was not a failure mechanism however.



Figure 4. Tunnel boring machine FM insert

Bucket Lip Inserts

Bucket lip inserts approximately 8” by 1” in size and 0.5” thick as shown in Figure 5 were fabricated and evaluated in hard sandstone under wet conditions. Tests were performed with The Robbins Group in Australia for over one year, during which time the inserts performed well and out performed ESCALLOY typically used for this application. These inserts were fabricated from WC with a 6%Co core and a 16%Co shell, in the FM architecture.



Figure 5. Bucket lip insert shown the individual tooth (right) with the FM compression fitted into the edge and as fitted into the bucket (left)

Hot Metal Extrusion Dies

A number of ceramic extrusion dies were made from Al_2O_3/Al_2O_3-TiCN FM compositions for the extrusion of hot brass as shown in Figure 6. A number of the dies failed during compression fitting into a heated metal holder but Metal Craft Extrusion Tools of Michigan were able to extrude approximately 6000' of brass as shown in Figure 6 without measurable signs of wear on the tool. This significantly outperformed any of the metallic dies evaluated. In addition, no break-in period was required as with metallic dies.



Figure 6. Al_2O_3/Al_2O_3-TiCN extrusion die for hot brass extrusion (left) with a 1" diameter. Extruded brass (right) - superior surface finish and dimensions over conventional metallic dies.

Ceramic Liners for Metal Pipes

Ceramic pipes were fabricated and metallic cases cast around the exterior to provide a design which could conceivably be used to transport highly corrosive, or erosive slurries as shown in Figure 7. The cylinders have not yet been evaluated but the hardness of the ceramic increases towards the interior showing that the ceramic has been placed in a small amount of compression due to the metal shrinkage on cooling. Low cost ceramic tubes are presently available commercially in lengths up to approximately 1m. These cylinders could readily be fabricated into pipes.



Figure 7. Ceramic-metal pipe for hostile slurries.

Due to the different electro-chemical nature of the ceramics it maybe possible to preferentially charge the surface so as to eliminate the build-up of scale, such as the silica scale which precipitate out under supersaturated conditions in geothermal brines [12]. Ceramics are typically inert and not electrically conductive. SiC, $MoSi_2$, TiB_2 and other ceramics are however conductive and can be introduced as a second phase to make the bulk ceramic conductive if necessary.

Impact Milling

Al_2O_3/TiCN monolithic components have been fabricated and evaluated in an impact mill produced by Aerosion, Alberta Canada and have shown significantly less abrasive wear than their metallic counterparts. Ore, crushed to approximately 0.5" in size is distributed between the "delta" ceramic shaped ceramics shown in Figure 8 and impacted at very high velocities onto the post ceramic parts which are rotating in the opposite direction. Particles are impacted at a velocity of over 600 ft/sec giving a reduction ratio of up to 700:1, and achieving a power efficiency of 12 to 20kW/tonne of material. The mill is extremely efficient and has a footprint of only 52".

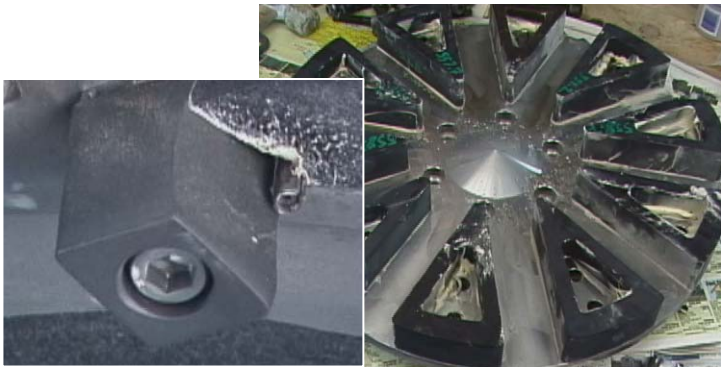

Figure 8. Ceramic plates (right) and posts (left) onto which the ore is accelerated and impacted causing a massive reduction in it's size.

Discussion and Conclusions

The high hardness and chemical inertness of ceramics make them materials of interest in high abrasive and corrosive environments such as geothermal drilling and processing. The poor damage and impact resistance usually exhibited by monolithic ceramics can be significantly improved through the fabrication of a fibrous monolithic architecture in which small islands of hard material and surrounded by a more ductile phase. This approach has been shown to offer a significant improvement in the damage tolerance leading to exceptional wear resistance. FM coated inserts consistently outperformed "monolithic" inserts for the same material system over 100s of field trials with poly crystalline diamond inserts. This technology is presently licensed to Kyocera in Japan and to Smith Tools in the US for oil and natural gas drilling applications. In low impact wear resistant applications such as bucket lips, extrusion dies and tunnel boring applications these FM structures performed well. Ceramics also offer considerable resistance to corrosive environments in hydrothermal and elevated temperature applications and may outperform many metallic systems in geothermal piping and tooling. These applications are presently being evaluated.

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