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Ceramic bead behavior in ultra fine grinding mills

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ABSTRACT

A preliminary review of the developing morphology of ceramic beads during extended operations in high energy stirred mills is presented.

Ceramic beads are produced from various formulations and processes; these certainly affect the cost of the media; but significantly, they impact the competence and performance.

Mills operate with a 'Working-Mix' or 'Seasoned-Charge'; invariably this means that worn beads of various sizes are present in the mill.

These beads can have effect on 'mill efficiency', 'overall media wear' and particularly 'mill wear'.

This study reports preliminary findings of wear profiles of typical ceramic media and some of the potential effects of extended use.

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1. Introduction

Saint-Gobain Zirpro has been instrumental in the development of ceramic media for ultra-fine grinding applications in stirred mills. The history and experience are long, dating back to the mid nineteen seventies. The company was in-fact established in 1971 to refine Zirconium Oxide to meet the Saint-Gobain Glass requirements for high performance refractories. The history of the Glass division is somewhat longer and it celebrated its three hundred and fiftieth anniversary last year.

Zirconia (Zirconium Oxide) and Zircon (Zirconium Silicate) turned out to be significant raw materials necessary to manufacture high quality ceramic beads. Initially beads were produced by a fusion process; the operation required high temperatures and the beads were formed in a molten state. The resulting product (ER120) was based on Zircon and had a density of 4.0 g/cc. The beads were round and non-abrasive and were ideal to replace the glass and natural sand products used in the burgeoning stirred or bead mill applications. A comparative increase in density of over

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50% was the important factor; greatly enhancing the productivity of the mills. Higher density media, such as steel (7.5 g/cc) for example, were largely discounted due to increased abrasion rates and contamination. Therefore ceramic technology was readily adopted by major industries, including pigments, paints and agrochemicals. The products proved to be extremely successful and remained at the forefront of the technology for over twenty years. Increased demands on milling technology were however inevitable and eventually faster, finer, more precise targets were expected. The industry responded with the development of new mill designs which operated at higher speeds, with higher energy and higher throughput rates. A new type of bead was required which would be tough and could withstand the new operating conditions. The result was the evolution of sintered beads, initially based on the same chemistry and having the same density as the fused products. These beads required low temperature forming before densification (sintering) at high temperature. The products proved to be suitable in many of the new applications, providing tougher beads with extended bead lifetimes. Zirpro again developed a class leading product (RIMAX) which gave exemplary performance in many varied fields for example cosmetics, inks and automotive coatings. Today the evolution has continued with the general acceptance of high density (6.0 g/cc) stabilized Zirconia beads as the media of choice (Hassall and Nonnet, 2007). The higher density provides the potential for superior and economic grinding and although initially expensive, the controlled wear provides an overall cost effective solution. Zirpro developed a premier product ‘ZIRMIL’ now widely adopted and widely used in the processing of the most demanding applications, such as pharmaceuticals and ceramics.

Mill design has also evolved to meet the ever increasing demands for ever more specialized materials and applications. At the forefront of these developments are two extremely different projects; the first is nano grinding of electronic materials and the second the ultra-fine grinding of ore bodies in the mining industry. For nano grinding, beads sizes of approximately 100 μm are required and potentially bead densities increasing beyond of 10 g/cc. For mining the environment is severe and beads must withstand high impacts from hard and large feed materials in dilute slurries.

In the nano application Zirpro has launched a derivative of the ZIRMIL range. Advanced ceramic technology and process engineering have enabled the production of 100 and 200 μm beads in industrial quantities at economic price levels. The material is currently under evaluation in extended customer trials. For mining a composite material MINERAX has been developed and successfully launched into the industry (Fig. 1). It is a tough composite material with a classic density of 3.9 g/cc and fully competent in all ultra-fine mining applications.

Fig. 1. MINERAX ceramic beads (*75% Alumina 25% Zircon*).

2. Materials and methods

2.1. Available beads type

Minerax is one of a number of ceramic beads available to the mining industry; many ceramic producers have launched products to meet the industry’s high volume demand. The range of chemistries, formulations and technologies employed are rather broad. Infact the only consistent factor is probably the size ranges offered; usually 2–3, 3–4, 4–5 and 5–6 mm. Although the formulations can vary significantly, fundamentally they are all based on three basic oxides, Silicon (SiO2), Aluminum (Al_2O_3) and Zirconium (ZrO_2); Silica, Alumina and Zirconia respectively. Non on the media are based on the pure forms, either due to suitability, ease of processing or cost. For example pure Silica bead is available but not at all suitable for the application. Pure Alumina product is possible but is difficult to process and would be prohibitively expensive. Zirconia is a special case where a stabilizing element is required to fix the material in its high temperature form. In the case of ZIRMIL, the addition of 5% Yttria produces a premier grade of product, very high performance but with a rather high cost. An alternative to Yttria is Ceria and similar stabilization can be achieved at a more affordable rate. Zirpro have developed an additional product for the mining industry ‘CERMIL’. It finds application in the mining industry in specific mill types where high bead densities are required.

The general range of media for the mining industry is actually more affected by the choice of available and cost effective raw materials; for example kaolin, Alumina and Zircon. From these the majority of formulations can be achieved. The raw material choice can also affect subsequent processing possibilities as the natural plasticity of kaolin can be exploited; alternatively additional organic plasticizers need to be added. The range of formulations and chemistry has significant effect on the nature and behavior of the bead. Density is the primary consideration (Becker et al., 2001) with products ranging from a low of 2.7 g/cc to a high of 6.2 g/cc. predominantly, however a mid-range of densities is preferred, in the range of 3.6–4.0 g/cc; this seems to suit the majority of mining applications. The physical properties of the beads are also linked to original formulation; factors such as hardness, toughness and strength are fundamentally affected. A point of consideration here might be an analogy with a ‘brick wall’; the individual grains of the bead (the bricks) have extremely good physical characteristic but the actual performance is more dependent on the binding agent (the mortar); it is often the consistency and make-up of grain boundaries of a bead which dictate its performance.

The processing of ceramic materials these days is more of an advanced engineering operation, but there certainly remains an element of the artisan or craftsman. An example of this is the relationship between the forming process and the final behavior and properties of the product. Ceramics are said to have a ‘memory’ and this refers to the fact that forces and stresses experienced in forming become manifest in the final structure of the product (Ford, 1967). For beads there are two main forming processes; dripping and granulation. The dripping process involves forming a plasticized paste which is extruded through fine forming nozzle. The process provides a high degree of homogeneity in the formed bead. This is important in subsequent firing procedures as the uniformity assist in grain growth and densification at high temperature. The main drawback of the process is the lack of uniformity in the final shape, beads often tend to be ‘tear drop’ shaped which is a potential problem when the bead is in use. The other