General Advancements in Zirconia Technology

Zircoa's approach to product, material development and application support will be described using an example of high performance milling media tailored to specific application requirements with an emphasis on QC testing, product consistency validation and application support tools.

Tab. 1
Typical mechanical properties for some media materials

	Steel	Glass	Al_2O_3	Zircon	Mg-PSZ	Ce-TZP	Y-TZP	ATZ	ZTA
Density [kg/m^3]	7800	2600–4400	3700	3800	5500	6250	6000	5300	4400
Hardness [GPa]	4–8	2–8	13–15	6	9–14	9–12	10–14	12–14	14–15
Strength [MPa] (approximate)	700	500–1200	500	200	600	650	1050	850	650
Fracture toughness [$MPa\ m^{1/2}$]	15	15	0,2–0,8	5	6–20	6–30	6–15	6–11	3–7

Introduction

Recent advancements in comminution technology are related to production of nanopowders and to large volume mineral processing. In these very different application areas, stirred high energy bead mills became the standard for particle size reduction equipment.

Main contributors to milling process efficiency are media type, mill wear and energy consumption. Optimization of milling efficiency places a set of stringent requirements on material properties and the shape of beads. Among them are: process specific optimum bead material density, high hardness/fracture toughness, smooth surface, low friction coefficient, spherical shape, high mechanical integrity.

Keywords
zirconia, zircon, comminution technology, statistical process control

Due to the high cost of raw materials used in nanoparticle production and very large volumes of beads required for the mineral processing equipment, quality control to assure consistency of the bead quality has become a key factor in maintaining high milling efficiency.

It is also highly desirable to develop tools for express assessment of the media condition during the operation of the mill for predictive maintenance and for prevention of catastrophic process interruptions.

In this paper, different media materials are compared in terms of their wear resistance and impact on mill wear. The effect of individual media shape and size distribution on milling efficiency is reviewed. Test methods for material property assessment will be described and customized image analysis capabilities for predictive milling process efficiency characterization will be discussed.

Beads material selection

Currently media is offered in a variety of materials as shown in Tab. 1. Their density varies from the densest steel to the low cost and low density glass. Depending on the application, steel can offer certain advantages for dispersing high viscosity products, however, steel use is declining due to contamination, corrosion and interference with downstream processing of the milled minerals. Glass media can be utilized for dispersing low viscosity products; however, it has very poor wear resistance and cannot be used for high energy milling of viscous slurries.

Among ceramic media, zirconia-based ceramics offer a combination of properties such as high hardness, fracture toughness, tailorable density range and chemical stability that make it an ideal mill media choice. The grade with the lowest hardness is zircon (zirconium silicate). It has relatively low density and strength and has a tendency for breakage and accelerated wear with prolonged use. The grade with the highest hardness is ZTA (zirconia toughened alumina). Selection of the media material is based on application process requirements, i.e., hardness of the media must be higher than the hardness

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of the mill feed material. Four types of zirconia based compositions were widely used over the years: magnesia partially stabilized zirconia (Mg-PSZ), yttria stabilized tetragonal zirconia polycrystals (Y-TZP), and ceria stabilized tetragonal zirconia polycrystals (Ce-TZP). All of these materials have varying microstructures as shown in Fig. 1.

Wear resistance of a media material is directly related to its microstructure. Dendritic zirconia phase surrounded by a glassy phase of zircon (Fig. 1 a) are the reasons for the inferior mechanical properties, often leading to preferential wear and breakage. Large grain sizes of Mg-PSZ (15–50 µm, Fig. 1 b) is the reason for abrasive bead and mill wear. Fine grain structure (<1 µm) of tetragonal zirconia compositions of Ce-TZP (Fig. 1 c) and Y-TZP (Fig. 1d) are the basis for superior wear resistance of these types of media. Since Ce-TZP is stable against low temperature thermal degradation, which plagues Y-TZP media at temperatures 200–300 °C, Ce-TZP is becoming preferred choice for applications requiring high density and preferred combination of hardness and fracture toughness.

Tab. 2 shows comparison between measured mechanical properties of several types of media with the different microstructures shown in Fig. 1. Finer grain sizes of Ce-TZP and ATZ media result in better hardness/fracture toughness combination as compared with ZTA media which exhibits larger grain size.

Higher hardness and fracture toughness leads to a significant reduction in both media and mill wear as shown in Tab. 3. All beads were tested under similar test conditions with platinum (Pt)-bearing ore as a feed slurry in a laboratory M4 IsaMill™. Wear rate of beads with a better microstructure and mechanical properties offer up to ~7× time improvements in the beads wear rate and ~ 3× reductions in the mill component wear.

Bead's surface condition also plays a critical role in assuring high wear resistance. Fig. 2 shows the effect of "smooth" (Fig. 2 a and b) and "rough" (Fig. 2 c) on the wear rate of beads tested with a mineral filler slurry. Beads with a "smooth" surface demonstrate ~½ of the wear rate of the beads with a rough surface.

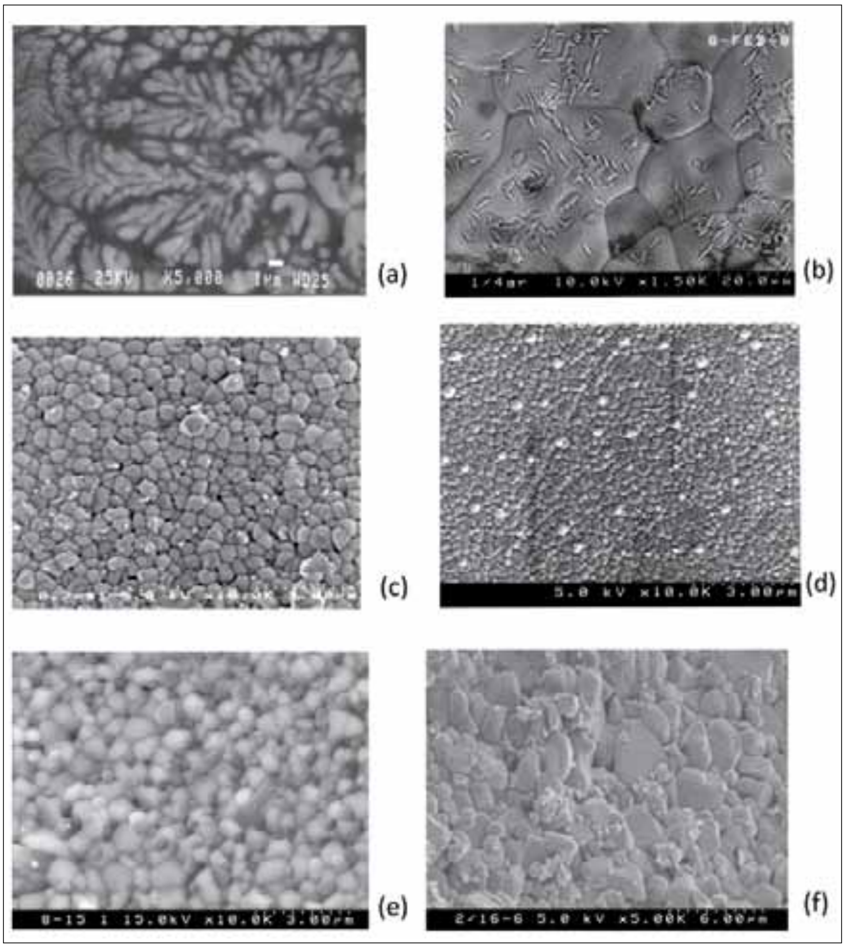

Fig. 1
Microstructure of different bead compositions:
(a) fused zircon, (b) Mg-PSZ, (c) Ce-TZP, (d) Y-TZP, (e) ATZ, (f) ZTA

Tab. 2
Measured mechanical properties of media shown in Fig. 1

Media Type	Grain Size [µm]	Density [g/cm³]	HV [GPa]	K_1C, [MPa*m$^{1/2}$]
ZTA	2,2	3,9	12,1	3,8
ATZ	0,8	5,3	12,7	10,5
Ce-TZP	0,5	6,2	11,5	11

Tab. 3
Wear rate test with Pt-bearing ore

Media Type	Bead Size [mm]	Tip Speed [m/s]	Normalized Wear Ratio	
			Bead Wear	Mill Impeller Wear
ZTA	2	11,4	1,0	1,0
ATZ	2	11,4	0,15	0,35
Ce-TZP	2	11,4	0,2	0,3

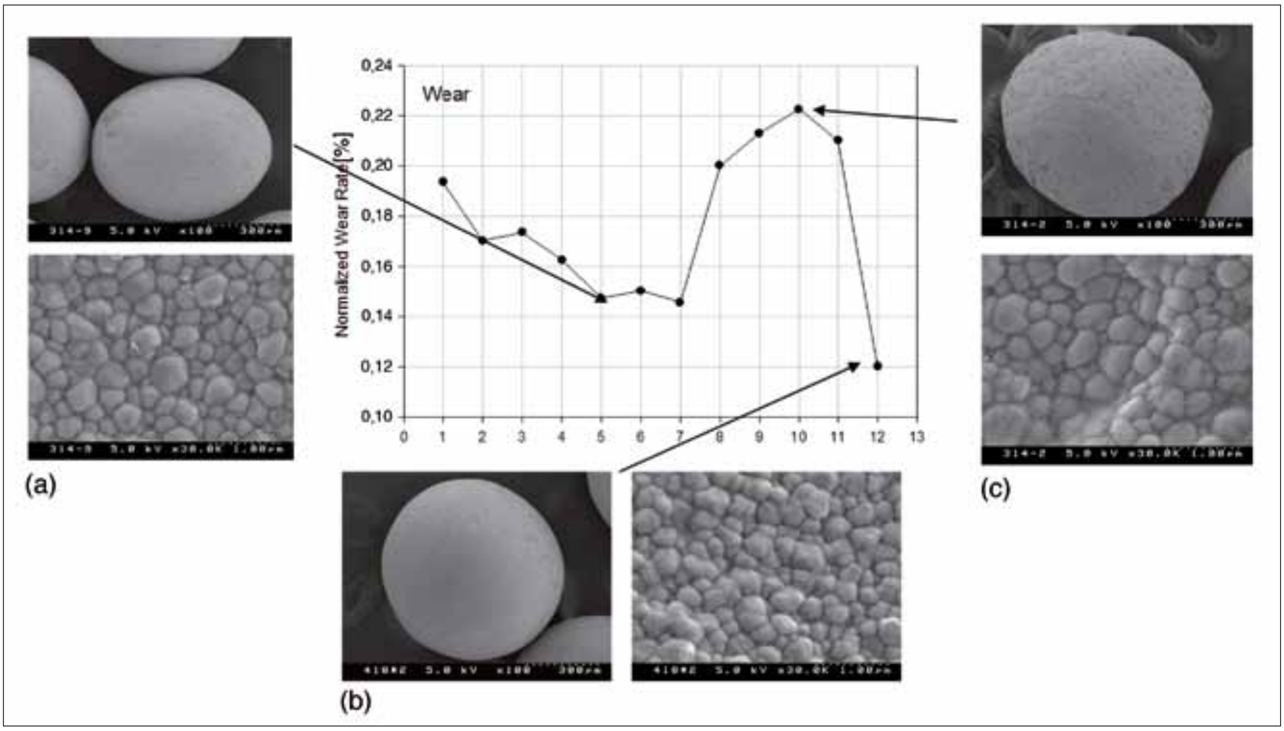

Fig. 2
Effect of the bead's surface roughness on the wear rate

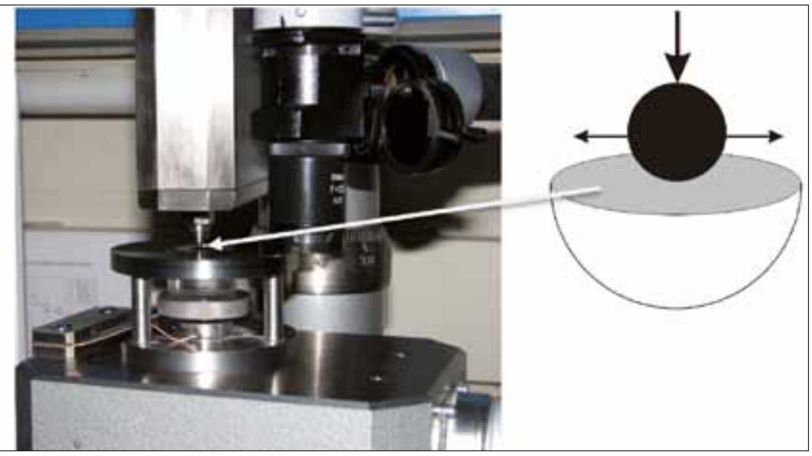

Fig. 3
Test setup for bead to bead friction coefficient measurements

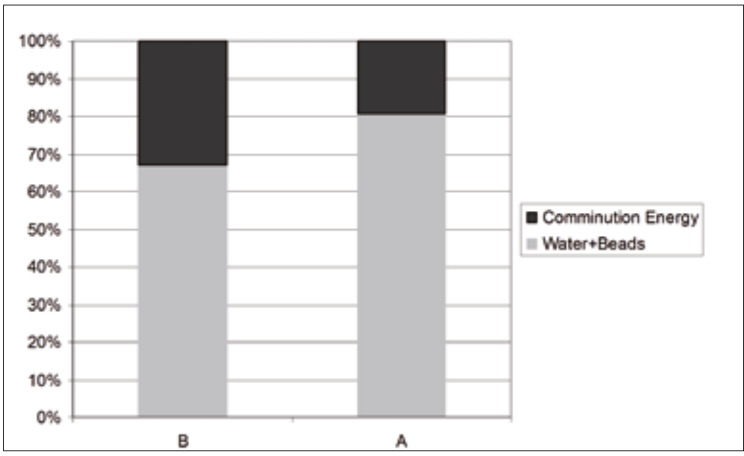

Fig. 4
Relative fraction of comminution energy in total mill power draw for ZTA (A) and ATZ (B) beads

Optimization of the comminution process is achieved by maximizing energy transfer during the individual particle breakage events [1] (which is related to bead size distribution and density) and minimizing friction related energy loses during mill operation [2].

Direct measurement of bead friction coefficient is a challenging problem. A custom made friction tester as shown in Fig. 3 allowed direct measurements of bead versus bead friction coefficient [3]. Tab. 4 shows friction coefficient measurements for fine-grained ATZ beads (~0,5 µm) and coarser-grained ZTA beads (>2 µm) in direct contact (dry), in water, and in the Pt-bearing ore slurry. In both test environments, material with a finer grain size shows a lower coefficient.

The lower friction coefficient of a finer grain structure results in more efficient distribution of the mill power draw. Relatively more energy is used for the actual comminution process versus energy needed for maintaining mill operational conditions without the product feed. Fig. 4 demonstrates that significantly improved (~20 %) energy utilization can be achieved using beads with lower friction coefficients. Since energy accounts for ~50 % of the operating costs in the mineral processing, and most of it is used during ore comminution, these realized energy savings presents significant opportunity for mineral processing efficiency optimization.

The lower friction coefficient of ATZ beads versus ZTA beads also contributes to reduced mill wear as seen from the test results in the Pt-bearing ore slurry shown in Tab. 3.

Additional optimization of comminution efficiency can be realized by optimization of bead size distribution. Comminution efficiency is a function of the bead density and the powder particle size in the feed slurry. Models capable of predicting particle size reduction ratios (disintegration rates) during a single pass through the mill have been developed [3–5].

Fig. 5 shows that for a specific particle size in the feed slurry, there is an optimum bead size resulting in the most efficient milling rates for a chosen bead density. This sharp optimum in the bead size distribution implies necessity of proper selection of the initial bead size distribution and it’s monitoring during use. Beads with sizes significantly smaller than the optimum size become an inefficient contributor in the comminution process and need to be removed from the mill load by screening.

Zircoa developed a user-friendly custom image analysis system that generates backlight two-dimensional projections of discrete beads placed on a glass slide (Fig. 6 a). The analyzed bead images (Fig. 6 b) are represented by an equivalent ellipse (ellipse with the same area as the projected area of a particle). Parameter descriptions for individual bead are shown in Fig. 6 b. An example of a narrow size distribution of as-manufactured beads is shown in Fig. 7.

Tab. 4
Friction coefficient measured for ZTA (Fig 1f) and ATZ (Fig. 1d) beads in water and Pt-bearing ore

Bead Type/Test Environment	Dry	Water	UG2 Slurry
ZTA	0,13	0,16	0,29
ATZ	0,12	0,13	0,24

To assist customers with the application support, a bead size monitoring system was developed.

Traditionally, mill media wear rate is evaluated by measuring media level in the mill, or by removing media and weighing it after a certain number of hours. Image analysis was used as an alternative approach to evaluate media wear and predict maintenance schedule requirements for the mill user. A mill operated for more than a year and small samples of media were taken from the grinding chamber, placed on the glass-slides and analyzed after 440, 1200, 1900 and 4100 h of mill operation [6].

Fig. 8 shows a linear decrease in the bead size over an extended utilization period. This linear reduction in bead size allows accurate estimation of the bead wear and can be used to estimate time for necessary predictive maintenance and avoid catastrophic process upsets due to penetration of the finer beads through retaining screens.

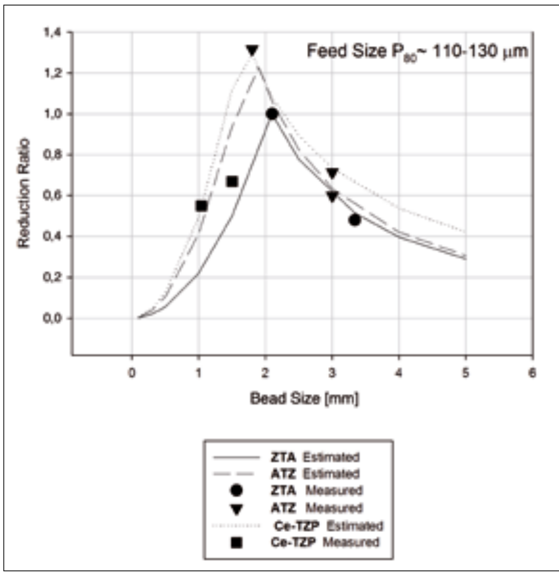

Fig. 5
Calculations of the feed particle size disintegration rates for media with different size and density versus test results

Through combination of measurements including bead size distribution, bead shape, and friction coefficients, mill power draw can be estimated. Fig. 9 shows that mill power draw can be accurately predicted from the bead surface area (total area of load of beads in the mill), shape factor (ratio between minimum and maximum bead axes) and the friction coefficient (a measure of bead surface condition or roughness) [7].

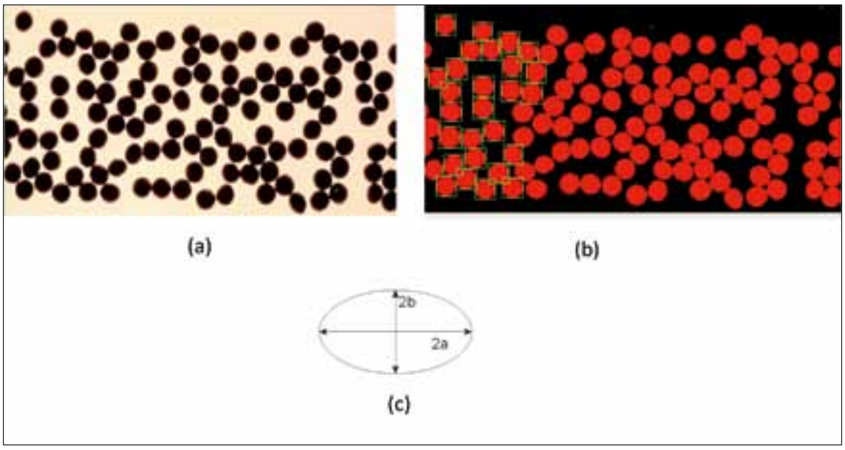

Fig. 6
Image analysis methodology

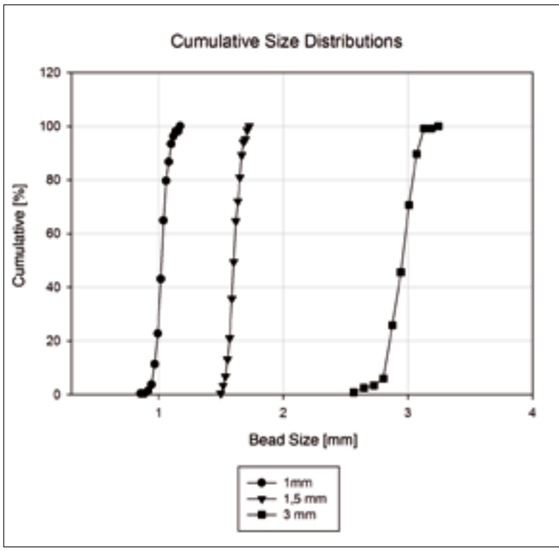

Fig. 7
As manufactured media size distribution

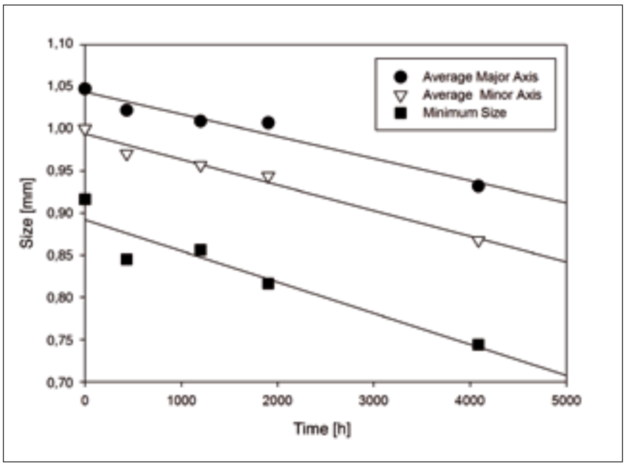

Fig. 8
Operational time dependence of the Ce-TZP bead's size measurements

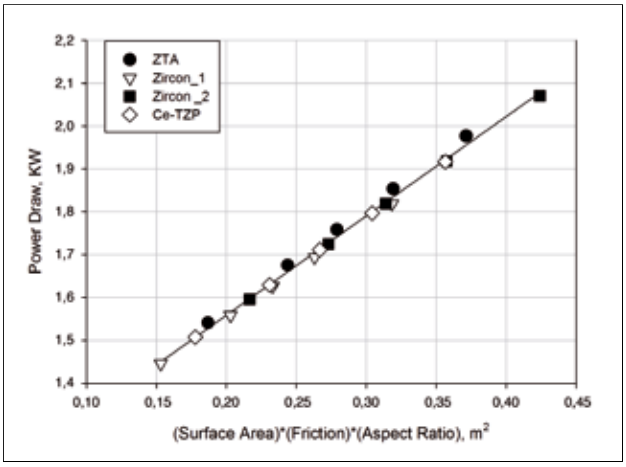

Fig. 9
Mill power draw versus normalized bead surface area

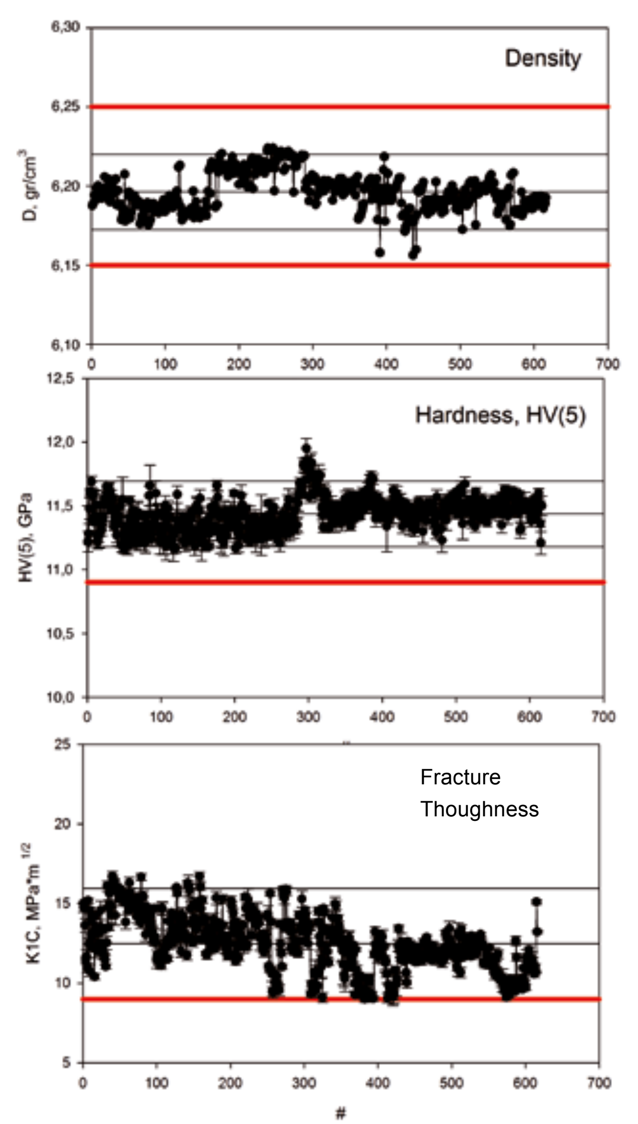

Fig. 10
Statistical process control of the bead manufacturing process

Mineral processing operations utilize a large volume of beads to fill mills with up to 10 000 l capacity. To maintain consistent process performance at the customer site, utilization of statistical process control tools for sampling and measurements of bead density, hardness and fracture toughness is becoming a necessary quality assurance procedure during bead manufacturing.

Fig. 10 demonstrates that during an optimized manufacturing process, bead density and mechanical properties can be controlled within narrow process limits.

Conclusions

1. Zircoa's approach to product, material development and application support that led to general advancements in zirconia technology was described by using an example of material development for high performance milling media.
2. Optimization of media material microstructure and bead surface smoothness results in significant reduction of the bead friction coefficient, bead and mill wear, and mill power draw.
3. Bead density and size distribution should be matched to the required process parameters.
4. Image analysis is a powerful tool for the comminution process efficiency monitoring as well as a predictive tool for mill power draw estimations.
5. Statistical process control of the manufacturing process is an effective quality control tool to assure consistent application performance.

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