The effect of chromia content on hardness of zirconia platelet toughened alumina composites

Meinhard Kuntz, October 22nd, 2014

1. Introduction

BIOLOX®*delta* is a zirconia toughened alumina ceramic (ZTA) for biomedical applications. As published, for example in 2001, the composition of BIOLOX® *delta* includes SrO, Y_2O_3, and Cr_2O_3 [1]. Strontia is included for the formation of platelets inside the matrix, which support the toughness of the material. Yttria is included in order to control the transformation mechanism of the zirconia phase.

According to [1], it was previously stated that the inclusion of chromia leads to improved hardness in a ZTA material. However, an earlier scientific study on this subject reveals a measurable increase in hardness only at a chromia content much higher than present in BIOLOX®*delta* [2]. Accordingly, further scientific literature suggests that the presence of chromia within a limited range does not influence the hardness of a ZTA material [3]. Further, internal CeramTec experiments have also observed no increase in hardness due to the presence of chromia. As such, CeramTec undertook a comprehensive examination in order to isolate the impact, if any, of chromia on hardness in BIOLOX®*delta*. Results of this analysis are described herein.

2. Description of test series

A test series of 4 ZTA variants was produced in the CeramTec laboratory. The 4 variants are identical in composition to BIOLOX®*delta*, except as to the content of chromia in 3 of the 4 variants. Table 1 gives an overview of the variants and the resulting grain size and density.

Chromia content	**0,00 %**	**0,14 %**	**0,32 %**	**0,50 %**
Grain Size Al_2O_3 [µm]	0,56	0,56	0,56	0,54
Grain Size ZrO_2 [µm]	0,28	0,27	0,29	0,27
Relative density	99,4%	99,4%	99,4%	99,4%

Table 1: Properties of ZTA variants. The acceptable range of chromia content for BIOLOX®*delta* is between 0,31 – 0,37%. Note that density is expressed relative to theoretical density of a 100% dense material as given in table 2.

Chromia content	**0,00 %**	**0,14 %**	**0,32 %**	**0,50 %**
Theoretical density [g/cm^3]	4,395	4,397	4,400	4,403

Table 2: Calculated theoretical density of the 4 ZTA variants.

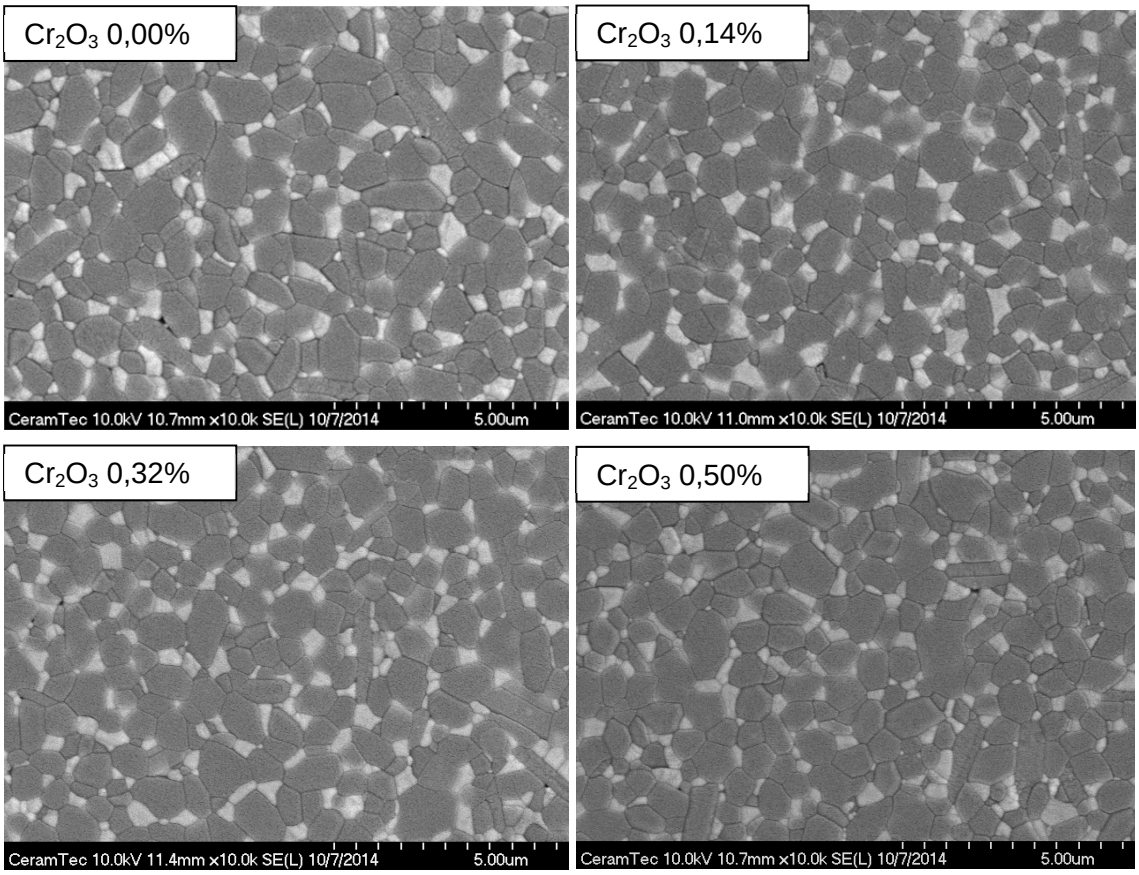

Figure 1: Microstructure of the 4 ZTA variants.

As shown in figure 1, the microstructure of the 4 variants is equivalent. All samples have the normal appearance of BIOLOX®*delta* on a microstructural level. Accounting for the natural minor scatter of material properties like grain size and density, these 4 variants are technically identical, with the exception of chromia content.

Hardness of ceramics is usually measured using the Vickers 4 sided diamond pyramid. It can be difficult to compare hardness values of historic and current data because the practice of hardness measurement according to the ISO standard [4] was revised occasionally. For high performance ceramics like BIOLOX®*delta*, it is today recommended to apply a test load of 9,807 N (*i.e.,* HV1). Lower loads like HV0.5 can lead to unacceptable measurement uncertainty due to the very small imprint. Higher loads like HV10 can lead to extensive crack extension at the corners of the imprint, which is also a source of inaccurate values. Historic data regarding hardness often used HV0.5 or HV10 measurements. It was thus decided to include 3 load levels in this study, *i.e.*, HV0.5, HV1 and HV10. As a reference, HV1 is the current standardized measurement.

Furthermore, the preferred unit of hardness values has been changed over time. Today, it is recommended to use the ratio of load vs. projected imprint area for the hardness value, which reveals Gigapascal [GPa] as the relevant unit. In historic data, a unitless number was preferred. Such numbers can be directly compared using the factor 0,009807. As an example, a hardness value of 2000 [-] equals 19,61 GPa.

Typically, hardness values are derived using the mean value of 5 imprints. For this study, 10 imprints for HV0.5 / HV10 respectively, and 10 imprints on 2 different bodies (*i.e.,* a total of 20 imprints) for the reference value of HV1 are performed. Such extensive statistical validation should lead to unquestionable results on the subject in this study.

3. Results

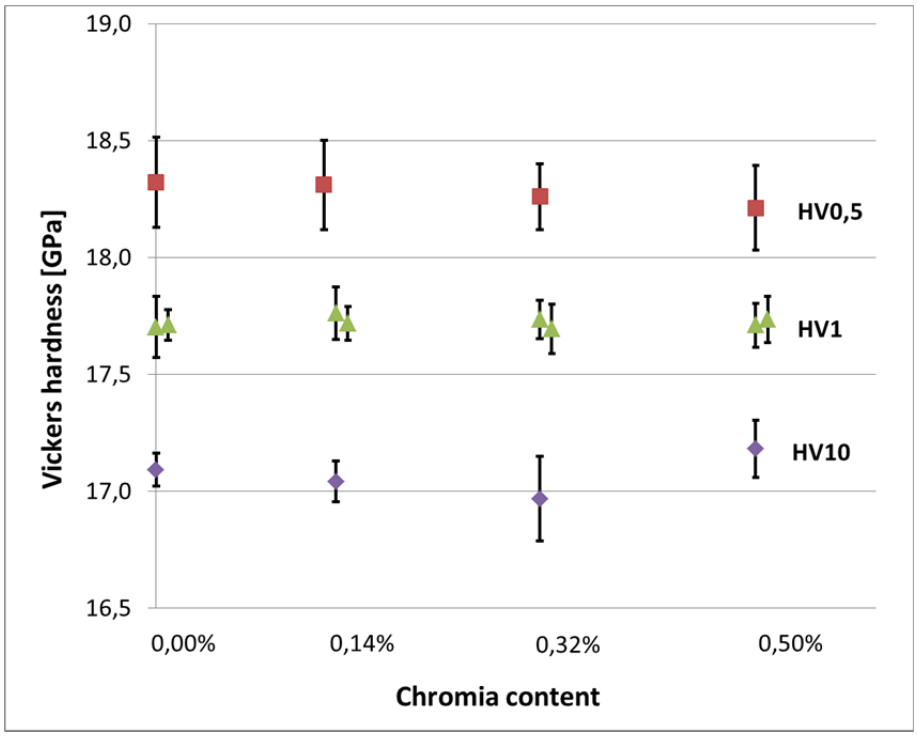

Figure 2: Results of the hardness measurements on the 4 variants.

Figure 2 shows the results of the analysis. Mean values ± 1 × standard deviation with the error bar are plotted. As it is already well known, the hardness values are higher at lower load levels of the indentation (at least within the load range of this study). For all load levels, no measureable influence of the chromia content to hardness is found. For the reference hardness value HV1 all results are virtually identical. The results are summarized in table 3.

Chromia content	**0,00 %**	**0,14 %**	**0,32 %**	**0,50 %**
Hardness **HV0.5** [GPa]	18,32	18,31	18,26	18,21
Standard Deviation [GPa]	0,193	0,186	0,141	0,181
Hardness **HV1** [GPa]	17,71	17,74	17,71	17,72
Standard Deviation [GPa]	0,100	0,095	0,095	0,095
Hardness **HV10** [GPa]	17,09	17,04	16,97	17,18
Standard Deviation [GPa]	0,072	0,088	0,181	0,124

Table 3: Results of hardness measurements

4. Discussion

These results demonstrate that the existence or non-existence of chromia in a ZTA material that is otherwise identical to BIOLOX® delta has no influence on the hardness of the material, at least in the range of the amount of chromia investigated here (0 – 0,5% by weight). For the study of [1], the load level HV0.5 was used which is not recommended today. This may be one source of inaccurate results due to high measurement uncertainty. In addition, the sample in [1] that contained chromia, also contained SrO, which was absent from the chromia-free sample. Unfortunately, the result of the study [1] of 2001 had been often quoted in publications referring to the material profile of BIOLOX®*delta*. However, the statistically substantiated test results discussed herein demonstrate that the chromia content of BIOLOX®*delta* does not measurably influence the hardness.

Literature

[1] W. Burger, H.G. Richter, *High Strength and Toughness Alumina Matrix Composites by Transformation Toughening and „In Situ" Platelet Reinforcement (ZPTA) – the New Generation of Bioceramics*, Key Engineering Materials Vols. 191-195 (2001), 545 – 548

[2] R.C. Bradt, *Cr_2O_3 Solid Solution Hardening of Al_2O_3*, Journal of the American Ceramic Society (1967) [5], 1, 54 – 55.

[3] G. Magnani, A. Brillante, *Effect of the composition and sintering process on mechanical properties and residual stresses in zirconia alumina composites*, Journal of the European Ceramic Society 25 (2005) 3383-92

[4] ISO 14705 *Fine ceramics (advanced ceramics, advanced technical ceramics) – Test method for hardness of monolithic ceramics at room temperature*