# A TRAVEL INTO CERAMIC PIGMENTS MICRONIZING

**Chiara Zanelli [1], Gülşen L. Güngör [2-3], Alpagut Kara [2-3], Magda Blosi [1], Michele Dondi [1], Davide Gardini [1]**

[1] CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici, Faenza, Italy

[2] SAM, Ceramic Research Center Inc., Eskişehir, Turkey

[3] Department of Materials Science and Engineering, Anadolu University, Eskişehir, Turkey

## ABSTRACT

An increasing number of ceramic tiles are decorated by inkjet printing, utilizing in most cases pigmented inks. These inks are manufactured by micronizing conventional ceramic pigments, starting from 3-10 μm in size and going down to a median diameter usually ranging from 0.2 to 0.6 μm. The theoretical framework predicts significant changes in both optical and fluid mechanical properties during such a size reduction of pigment particles. However, not all the expected advantages occur and still unanswered questions concern colour strength and particle size distribution of micronized pigments, as well as efficiency and actual yield of the milling process. The present contribution is thought as a travel along progressive steps of pigment micronizing, that is aimed at disclosing what happens in terms of particles size, shape and composition in the submicrometric field. For this purpose, industrial pigments were selected to represent crystal structures with different density, hardness, cleavage and fracture toughness: Cr-Sb-doped rutile (orange-yellow), Co-Cr-Fe-Mn-Ni spinel (black), and V-doped zircon (turquoise). Pigments were micronized in a pilot plant (Netzsch Labstar LS1) keeping carrier, solids

load, type and concentration of dispersant, rotation speed, amount and size of grinding media, and milling time under control. For each pigment, sampling was carried out at increasing milling time in order to get "instantaneous pictures" at progressive stages of micronizing. Pigments were characterized for particle size distribution (laser diffraction and dynamic light scattering), particles morphology (SEM), phase composition and unit cell parameters (XRD-Rietveld), and colour after application in glazes for porcelain stoneware tiles fired at 1200°C (CIE L*a*b*). Preliminary results highlight a different behaviour during micronization: the milling efficiency decreases from zircon to rutile to spinel, in partial agreement with literature data. Crystal structural and optical features are substantially changed once pigment particles turn into submicronic size. A gradually lower particle dimension is accompanied by increasing frequency of lattice defects (inferred from variation of unit cell parameters) and sometimes amorphization. The occurrence of the amorphous phase may significantly reduce the pigment yield with loss up to 75% by wt. These structural changes are associated to decreasing colour strength and increasing brightness through the submicrometric field, as outlined by zircon pigments taken as an example. Microscopic observations reveal changes in particles size and shape during micronization that are able to influence both pigment milling yield and ink performance.

## 1. INTRODUCTION

Drop on Demand Ink-Jet Printing (DOD-IJP) is increasingly utilized to decorate ceramic tiles worldwide[1]. The inks used in DOD-IJP contain in most cases ceramic pigments as colorant[2-3]. These inks are currently prepared by high-energy ball milling that reduces the pigment size from micrometric to submicrometric (the target being 0.2-0.5 μm as mean diameter and 99% below 1 μm)[3-4]. Although a detailed know-how exists on ink properties for DOD-IJP (viscosity, surface tension, Z-potential, fluid mechanics numbers) that govern the behaviour during jetting, spreading and storage[5-6], little is known about what happens to pigments during micronization[7]. There is a large body of literature on mechanochemical synthesis/alloying by using high-energy ball milling, including some extensive reviews[8-9]. Most papers deal with metals and alloys; much less knowledge is available on oxide behaviour and substantially does not cover the structures used for ceramic pigments[10].

The theoretical background predicts changes to optical properties of micronized pigments: light absorption should increase moving from micrometric to nanomicrometric sizes, while scattering should peak at about half the light wavelengths[11], i.e. 200-400 nm or 0.2-0.4 μm, more or less the target size for pigmented inks. However, not all the expected advantages occur and still unanswered questions concern colour strength and particle size distribution of micronized pigments as well as efficiency and actual yield of the milling process[4].

The aim of the present work is to follow what happens to pigments during micronizing and successive steps of the tile manufacturing process. For this purpose, three archetype structures were considered representative of ceramic pigments used for DOD-IJP: spinel, zircon, rutile. Industrial processing was simulated at the laboratory scale, particularly high-energy ball milling, glaze application and firing. In-depth characterization of pigments was performed at every processing step. In this preliminary outline, zircon inks are taken as an example, comparing results with the other two pigment structures.

## 2. EXPERIMENTAL

Industrial pigments were selected to represent crystal structures with different density, hardness, cleavage and fracture toughness: turquoise V-doped zircon (TZ); black Co-Cr-Fe-Mn-Ni spinel (BS); orange-yellow Cr-Sb-doped rutile (OR).

The micronization process was simulated in a pilot plant (Netzsch Labstar LS1) keeping carrier (distilled water), solids load (30% by wt), type and concentration of dispersant (no or 0.5% by wt Darvan C), rotation speed (1000, 2000 or 3000 rpm), amount and size of grinding media (0.4 or 0.6 mm) and milling time (up to 120 min) under control. For each pigment, sampling was carried out at increasing milling time in order to get "instantaneous pictures" at progressive stages of micronizing.

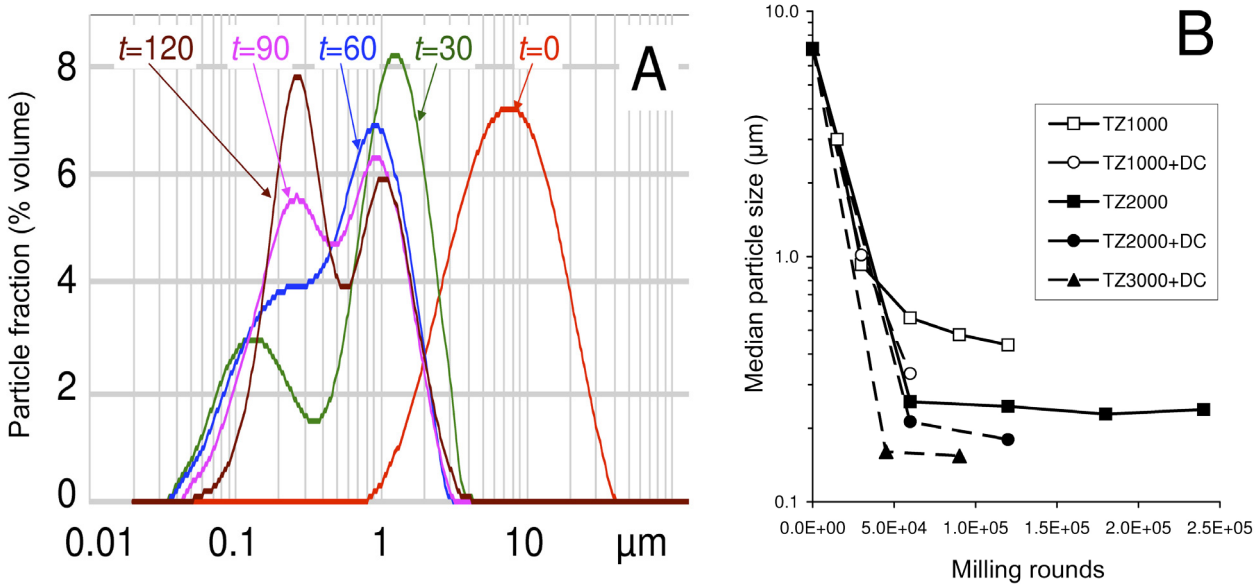


*Fig. 1. Particle size distribution of zircon inks (A) after increasing milling time (t=minutes) and (B) at different rotation speed (1000, 2000 or 3000 rpm) with (+DC) or without dispersant.*

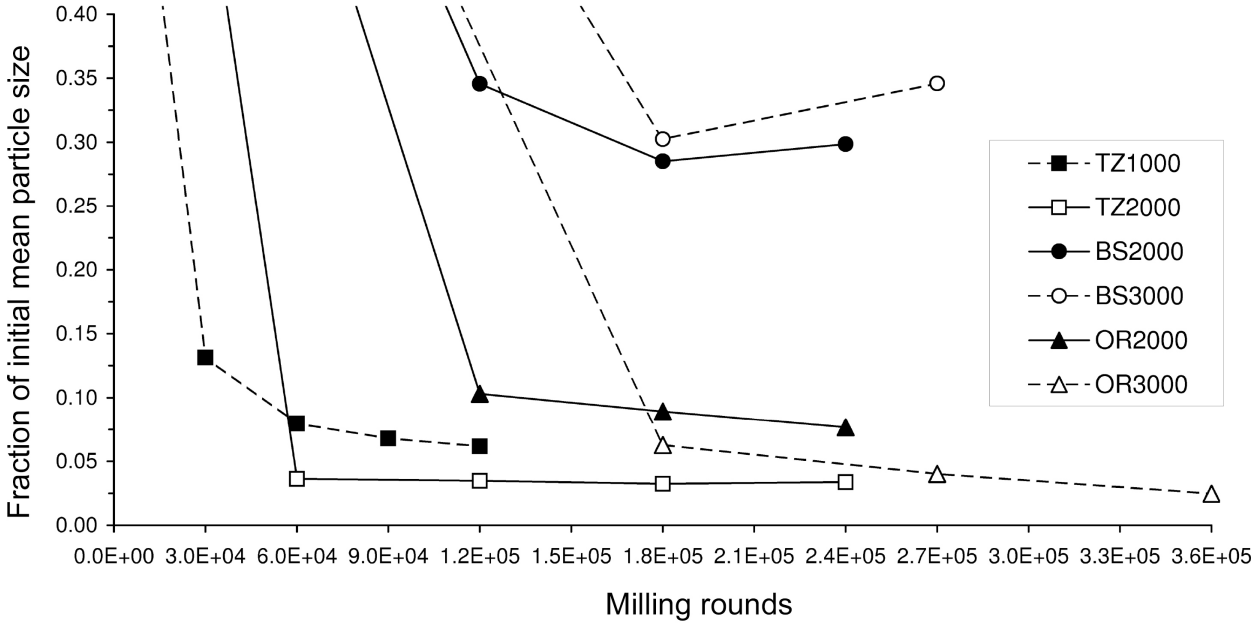


*Fig. 2. Milling curves of zircon (TZ), rutile (OR) and spinel (BS) inks at different rotation speed (1000, 2000 or 3000 rpm) without dispersant.*

Pigments were characterized determining the particle size distribution by laser diffraction (Malvern Mastersizer 2000) and dynamic light scattering (Malvern Nanosizer); particles morphology by SEM (Carl-Zeiss EVO-50 VP); phase composition and unit cell parameters by XRD (Bruker D8 Advance) with Rietveld refinement (GSAS-EXPGUI); optical properties by DRS (Perkin-Elmer Lambda 35); colour by CIE L*a*b* coordinates, where $C^*=(a^{*2}+b^{*2})^{0.5}$, after application in glazes for porcelain stoneware tiles fired at 1200°C (Hunterlab Miniscan MSXP4000).

## 3. RESULTS AND DISCUSSION

**Micronization** proceeds through a progressive breakdown of pigment crystals from the initial size to the minimum dimension achievable with the given set of milling conditions. During most of this process, a bimodal particle size distribution is observed with two maxima around 1 μm and 0.3 μm, respectively (Fig. 1A). Milling curves exhibit a rapid drop of median particle diameter until a critical dimension is reached (corresponding to about 40,000 to 60,000 rounds in the case of zircon inks). Any further particle size reduction beyond this critical point occurs with a very slow rate, causing an abrupt slope change (Fig. 1B).

These experiments demonstrate that the milling efficiency depends considerably on the processing conditions, even if the slope of the median particle diameter in function of milling rounds is approximately the same in the early stage (Fig. 1B). What significantly changes is the critical particle size that, keeping constant all the other variables, turns smaller for increasing rotation speed (at the same number of rounds) and once a dispersant is used (at the same rotation speed). These results are somehow expected as milling energy is not linearly increasing with rotation speed and dispersant improves the process efficiency by dumping the ink viscosity[8].

The same behaviour was observed by micronizing spinel and rutile inks, though with different critical sizes and milling times (Fig. 2). In particular, the rutile inks approached the same critical size of the zircon ones, in terms of fraction of the initial median particle diameter, but after longer milling times. Furthermore, they exhibit a slightly faster milling rate beyond the critical point. In contrast, a reduction of the initial particle size is less pronounced in the spinel inks, though milling times are approximately the same of rutile inks. Overall, the micronizing efficiency of inks is in the increasing order: spinel < rutile < zircon. This order does not correspond to Mohs hardness, fracture toughness, elastic moduli, or Bond work index of the crystal structures under investigation, but seems to match the difference in terms of Vickers hardness.

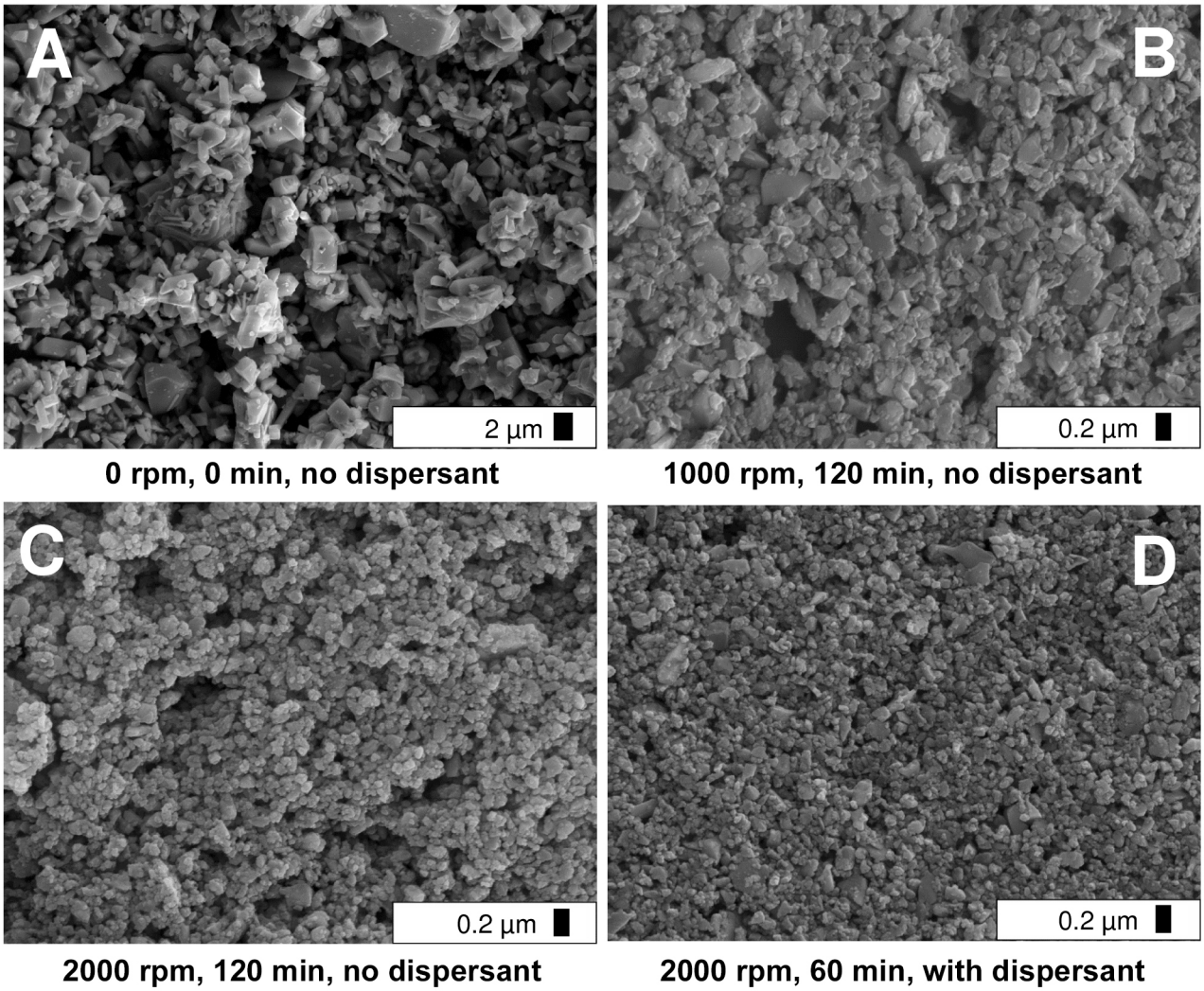


*Fig. 3. Microstructure of zircon ink during micronization.*

**Microstructural observations** confirm the path of particle size change during micronization, as outlined by particle size analyses, including a bimodal particle size distribution (Fig. 3). The milling process induces a strong variation of crystal shapes: in the case of zircon inks, from predominantly prismatic shapes in the starting powder (Fig. 3A) to irregular fragments with a wide range of morphologies (Fig. 3B) until mostly isodiametric grains are obtained (Fig. 3C and 3D). This is in fair agreement with the fracture behaviour of zircon, which breaks down with indistinct cleavage and conchoidal parting.

From the SEM micrographs, it is clearly appreciable how faster speed gives rise to more uniform particles size and shape at the same number of rounds (Fig. 3B versus 3D). A dispersant can be very effective to improve grinding, even with half the number of rounds for the same rotation speed (Fig. 3C versus 3D).

These observations can be to a good extent replicated for rutile and spinel inks, besides each crystal structure exhibits its own fracture behaviour. Overall, micronized pigments mostly consist of angular fragments, with many sharp points and scarce rounded grains.

**The phase composition** of the industrial zirconium silicate pigments contain, along with zircon, some unreacted precursors: baddeleyite (monoclinic $ZrO_2$) and quartz ($\alpha$-$SiO_2$). This initial composition is substantially retained during early micronizing stages, until the critical point in milling curves is approached (about 60,000 rounds in Fig. 4). Beyond this limit, a partial amorphization occurs at expenses of zircon (and quartz) though baddeleyite seems to be less affected. The amount of such an amorphous phase rapidly reaches 20-25% by weight, depending on milling conditions.

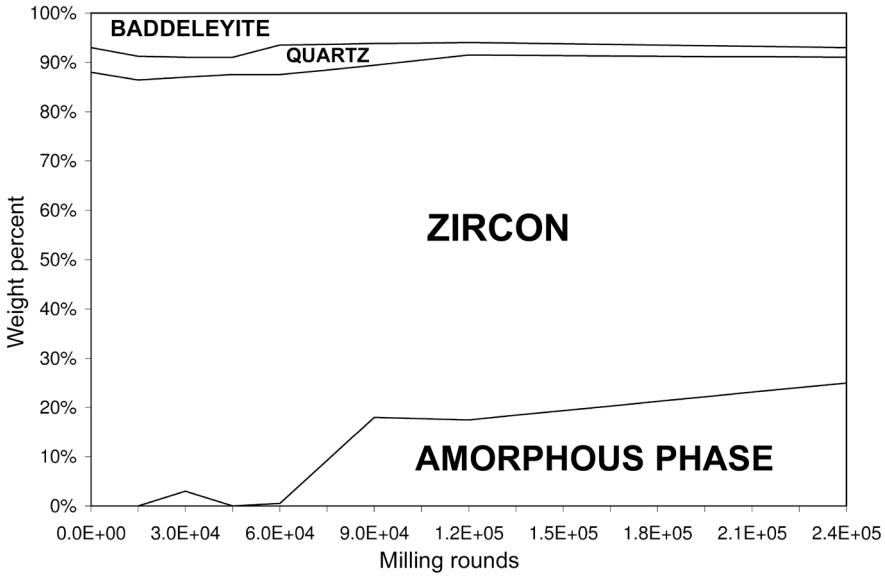


*Fig. 4. Phase composition of zircon ink during micronization.*

In spinel inks, amorphization also occurs beyond the critical point (approximately 120,000 rounds, Fig. 5A) and the amount of amorphous phase ranges in between 20% and 40%. In the case of rutile inks, the formation of amorphous phase was observed even in the early stage of micronization and its amounts may approach 75% after prolonged milling (Fig. 5A).

Although an amorphous phase development during high-energy ball milling was already claimed for oxide systems[10], this is the first report of an extensive amorphization of ceramic pigments occurring during the micronizing process. In this framework, the dispersant may play an important role in the amorphization kinetics and investigations are in progress to better understand this aspect.

Micronization induces, along with amorphization, damages to the crystal structures, which are reflected by changes in the unit cell parameters of pigments. Normalizing the unit cell volume (i.e., starting pigment = 1) it is possible to compare zircon, rutile and spinel inks.

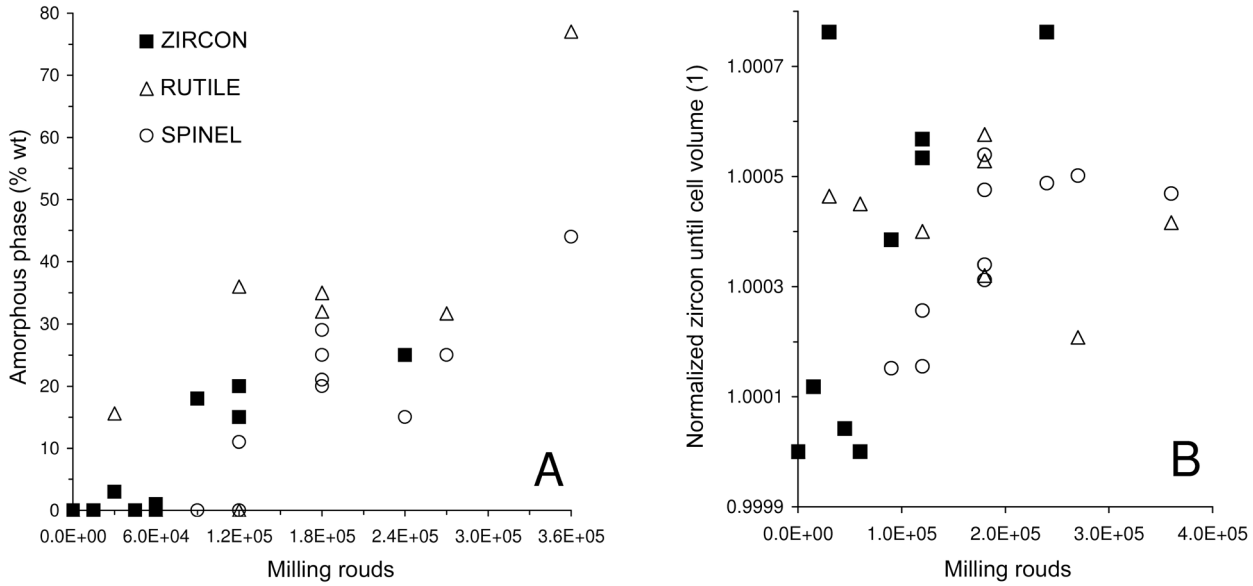


*Fig. 5. Effect of micronization on zircon pigment: A) amount of amorphous phase formed and B) change in the normalized unit cell volume in function of milling rounds.*

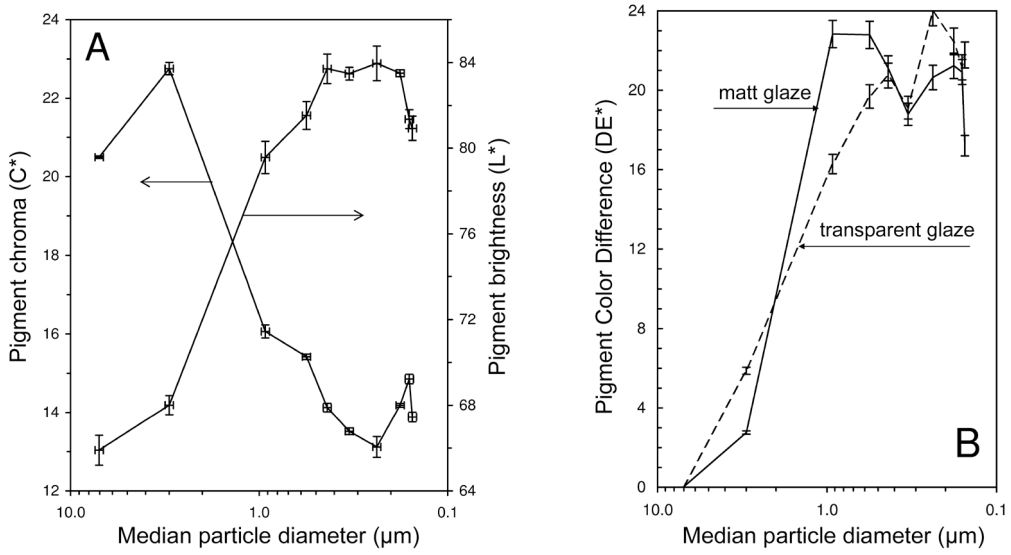


*Fig. 6. Colorimetric parameters of zircon ink in function of pigment particle size: (A) before firing and (B) after firing (ink applied on glazes).*

In all cases, a progressive increment of unit cell volume is observed with milling time (Fig. 5B). It is thought to be an effect of cumulative damages to crystal structures, by introducing defects or highly strained zones at the crystal edges. These preliminary data suggest that zircon pigment underwent a rate of damaging (i.e. the slope of unit cell volume versus milling rounds relationship) that is faster than spinel. Rutile pigment does not exhibit any clear dependence of unit cell volume with milling rounds: the crystal structure appears to be significantly "relaxed" already after the first step of micronization and this volume is more or less retained with further milling (Fig. 5B).

**Ink colour performance** is heavily affected by the micronizing process, as shown by changes of colorimetric parameters after increasing milling times before and after application on porcelain stoneware glazes (Fig. 6).

According to the theoretical background, light absorbance is increased when the mean particle size is reduced from 7 to 3 μm, though this gain is limited in zircon inks. However, a conspicuous deterioration of colour performance is observed once the pigment size turns into the submicronic field (Fig. 6A). It is witnessed by both the drop of chroma, corresponding to an increasingly less saturated colour, and the higher brightness, due to enhanced light scattering. Interestingly, brightness exhibits maximum values in the 0.2-0.4 μm range that matches the predicted scattering peak at half the incident light wavelength.

Also spinel and rutile micronized pigments suffer from changes in the colour performance, but with different trends with respect to zircon pigment, as a consequence of their own mechanisms of crystal fracture and damaging, and eventually amorphization.

The behaviour during firing was expressed in terms of colour difference with reference to the zircon pigment before firing (Fig. 6B). It is evident the conspicuous colour change that occurs while the pigment particles are gradually reduced from the initial diameter down to submicrometric size. Most interestingly, this loss of colour strength occurs in the early stage of micronization, despite an improvement was observed in the pigment before firing, and no significant colour change was revealed for further size reduction in the submicronic field.

## 4. CONCLUSIONS

High-energy ball milling of inks for digital decoration is able to efficiently reduce the pigment dimension to submicronic sizes, but it may induce significant differences in the ink properties, depending on processing conditions.

Micronization proceeds through a probabilistic breakdown of pigment crystals by a fast comminution rate in the early stage and a very slow rate beyond a critical point. This produces a bimodal particle size distribution with a tail of coarser grains that is difficult to be kept under control. These circumstances may induce to prolong milling times to fulfil the target of 99% of submicronic particles, but caution is needed because of damages that micronizing cause to the crystal structure of pigments. Changes to unit cell parameters presumably reflect the formation of defects and highly strained zones in the pigment lattice. An important loss of colorant occurs by amorphization, which can easily attain 20% to 40% of the initial pigment amount at a median particle diameter around 0.3 μm.

The ink colour performance is strongly dependent on particle size and phase composition. A conspicuous deterioration of colour strength stems from pigment amorphization, and faster pigment-glaze reaction kinetics are promoted by submicronic sizes.

Therefore, the detailed know-how on pigment behaviour during micronizing is the key point to improve the technological properties of inks for DOD-IJP of ceramic tiles. Further investigations are in progress to comprehend in-depth both phenomena occurring during micronizing and mechanisms governing the ink behaviour.

## 5. ACKNOWLEDGEMENTS

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