microcrystalline glazes

by Ryan Coppage, PhD and Jenn Wicks

While most envision crystalline glazes featuring big, beautiful crystals, luscious drips, and temperamental behavior, there is another side to them, namely microcrystalline glazes. These are characterized by smaller crystals and subtle changes in surface color and texture. They don't require complicated firings, and there's no need for glaze-catch dishes.

Define the Terms:

Crystallization: A precipitation (falling out) and growth of ordered material from a glaze base. The materials that promote crystallization in glazes are zinc, calcium, magnesium, titanium, or another metal oxide.

Glaze Matrix: The glaze solution, which is often silica blended with various feldspars and fluxes to lower its working temperature and alumina to add stability to the melt and make its coefficient of expansion similar to that of clay.

Microcrystalline: Crystallization that is more focused on multiple nucleation sites (more net crystals that are smaller) and less emphasis on growth of those individual crystal sites.

Nucleation Sites: A site where material first falls out of a glaze solution, forms the center of a crystal, and then other materials start coordination around it and expanding in ordered layering, forming a visible crystalline structure.

Opacifiers: Materials added to a glaze to make it opaque (not transparent): tin oxide, titanium dioxide, etc.

Precipitation: A pseudo phase change in which a solute material becomes separated from a solution and falls out.

Saturation: A phenomenon that occurs when a solute has reached the maximum quantity that can be dissolved in a given solution, which is temperature dependent. More often than not, hotter temperatures equate to more solute dissolved.

Saturation Point: The point at which no more solute/analyte can dissolve in a particular solution or mixture at a given temperature. This quantity changes with temperature.

Microcrystal Formation

The simplest metaphor for glaze crystallization (1) is to imagine a glaze as a glass of water. You know that you can put some amount of salt or sugar into it and that electrolyte dissolves. As you heat the water up, you can add more salt or sugar. Eventually, no more dissolves and you have reached the saturation point. Then, as the water cools back down, the excess salt or sugar, beyond the saturation point of the water, will crystallize on the surface of the glass or at a seed point known as the nucleation site. As the glass of water continues to cool, the saturation point of the salt or sugar continues to drop, forcing more of it to fall out of the solution and deposit on the started crystals. Eventually, the glass of water reaches room temperature, any amount of salt or sugar beyond the saturation has precipitated out and deposited on the nucleation sites, growing crystals. If you substitute salt or sugar in this metaphor with known crystallizers in ceramics (zinc, magnesium, calcium, or titanium) and replace the water with a glaze, you have a recipe for crystallization, albeit large or small. Crystallization, whether in glazes or solutions, is simply the formation of a precipitate.

Similar to that glass of water, precipitates form when a glaze solution is oversaturated, causing solids (i.e. crystals) to nucleate out of the glaze melt (2). In the case of microcrystalline glazes, small bits of titania, rutile, and/or zinc/magnesium oxide precipitate and form groups of tiny crystals within the glaze matrix. The difference between typical crystallization and microcrystalline formation is

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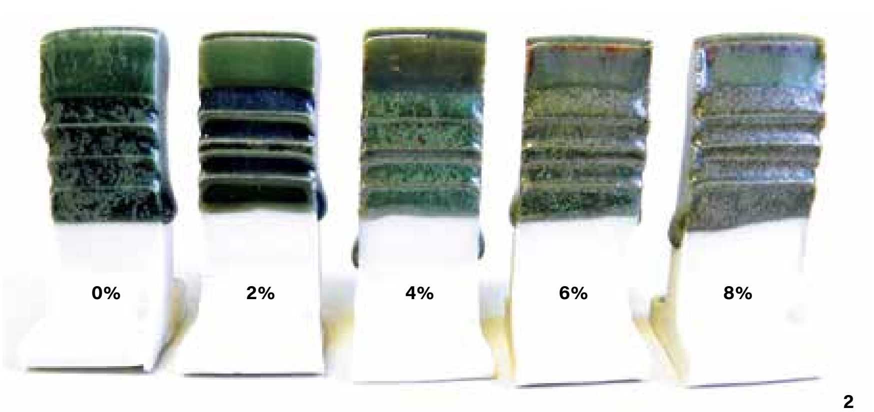
1 A mug thrown with Standard 213 clay body, glazed with 6% titanium dioxide added to the base Microcrystalline Glaze recipe and fired to cone 6.



2

2 Tiles with the Microcrystalline Glaze base. Titanium dioxide is omitted on the tile at the far left, then added in 2% increments up to 8% and fired to cone 6 in oxidation.

observed in recipe. Macrocrystalline recipes contain approximately 25% zinc oxide and form large zinc oxide crystals that grow as the glaze cools. They must also be incredibly fluid and runny to allow for the crystals to freely grow, thus the need for catch basins and difficulty in firing. Macrocrystalline recipes have multiple hold and ramp segments to their firing schedules. Different schedules yield different crystal growth sizes and patterns. These recipes were formulated for normal, medium, or fast cone-6 ramp schedules in a Skutt 1027 electric kiln with a digital kiln sitter.

Glaze Theory

A lot of this comes down to mixing a simple glaze base and adding known crystallizers—specifically in amounts above their saturation points. Titanium dioxide reaches saturation at 3–4% and starts to precipitate out at/above 4%. Rutile reaches saturation at around 5%, because in addition to titanium dioxide it is 20% iron content by weight. The best way to determine a material's saturation point is to do incremental tests.

The three main materials that make up any glaze are silica (the glass former), fluxes (lower the melting points of the silica to make it more easily workable/meltable), and alumina (a stabilizer, adjusts the glass to be compatible with ceramic surfaces). Beyond this, there are colorants, opacifiers, crystallizers, and other additives.

In this case, titanium dioxide, a known crystallizer, was added to a microcrystalline glaze base (containing calcium, zinc, and magnesium oxides as well) that was formulated to precipitate small crystals (see recipe below). Without any titanium dioxide, beautiful silvery zinc oxide microcrystals are formed on the glaze surface. As titanium dioxide is added and then increased up to 8%, increased crystallization can be seen on the tiles, which changes the glaze's color, opacity, and surface texture. Microscopically, the crystals start out a silver color, turn tan, then copper, and end as a medium red, with bulk crystallization on the surface of the glaze (3). Personally, I found an addition of 4–6% titanium dioxide to be ideal.

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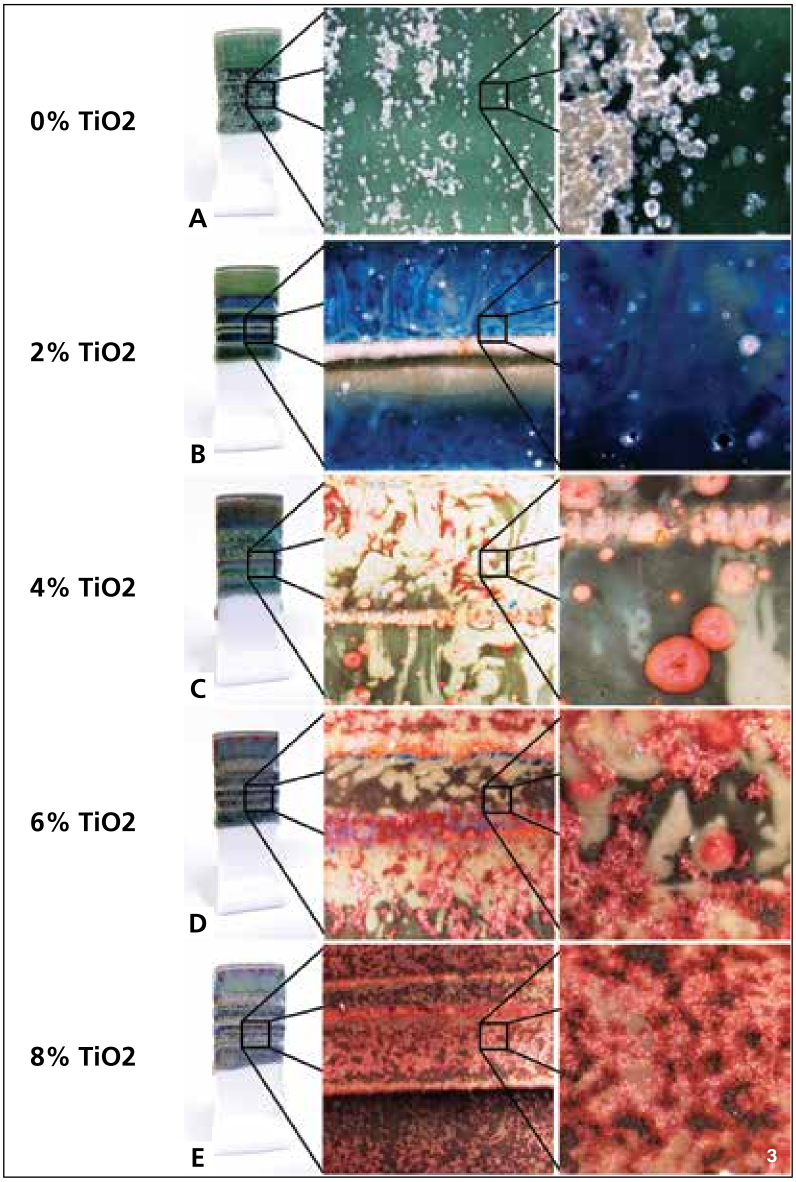
MICROCRYSTALLINE GLAZE

Cone 6 Oxidation

Magnesium Carbonate	6 %
Talc	6
Whiting	14
Zinc Oxide	6
Custer Feldspar	52
EPK Kaolin	6
Silica	10
	100 %
Add: Copper Carbonate	5 %
Titanium Dioxide	2–8%

Acknowledgements for the origin of this recipe go to Ivan Albrecht at the University of Miami. Titanium dioxide was added in the following increments: 2%, 4%, 6%, and 8%. If titanium dioxide is omitted, silvery zinc oxide microcrystals are formed on the glaze surface (see 3A). The microcrystalline glaze is a gorgeous blue with purple or gold crystals in this same series of experiments when substituting 1% cobalt carbonate instead of 5% copper carbonate.



3 Magnification of tile surface as incremental amounts of titanium dioxide are added. Percentages of titanium dioxide from top to bottom: 0, 2, 4, 6, and 8%. Imaged with an AxioCam MRc Zeiss 12-150x microscope.

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