copper red nanoparticles

by Karthik Lalwani, Michael Leopold, PhD, and Ryan Coppage, PhD

Copper carbonate makes the most notorious and vibrant of red glazes—and often only in reduction firings as a very delicate and precise schedule is required to obtain a crisp, crushed-strawberry-like red. Did you know this same phenomenon can happen in oxidation firings too?

Define the Terms

Electron: A subatomic particle of an atom that flows freely in metals, allowing for current or conductance, as well as for surface plasmon resonance (SPR) light properties to exist.

Nanoparticle: A small particle between 1 and 100 nm in size, of which these often interact with light through surface plasmon resonance to create various color phenomena.

Surface Plasmon Resonance (SPR): The phenomenon of light striking a small metal particle and exciting electrons on the surface so that electrons oscillate around the particle, such that the energy required to excite and move them (determined by particle diameter) is responsible for the wavelength of light absorbed (and thus their color).

TEM (transmission electron microscopy or microscope): A high-end microscope that works in the following way. Instead of focusing light, a series of electromagnets focus an electron beam generated from a filament at the top of an instrument to image materials on the nanometer scale—with dimensions on the scale of $1x10^{-9}$ meters.

Copper Reds

Like a few other technical ceramics folks in the field, I have openly mistaken copper reds as the mineral Cuprite (Cu_2O). This is even mentioned in my first ever *Ceramics Monthly* article—"Reduction Misnomer."[1] A few kind souls have pointed out that I was incorrect. To be fair to those of us who have made this mistake, most glaze colors and mechanisms are identical to mineral colors and mineral-color mechanisms. Copper red is different though.

Figure 1: Mug thrown with Laguna Frost, glazed with Poppyfield Glaze, and fired to cone 6 in oxidation.

Copper reds are actually very small particles of zero-valent (uncharged) copper metal, around 5–30 nanometers or so in size, that stabilize in a glaze and absorb and scatter light to create their brilliant red colors.[2, 3] It has only recently become known that these are nanoparticles, which require specialized microscopy (TEM) to properly image and characterize.

Silicon Carbide

Traditionally, copper reds are formed in a reduction kiln. They require the Cu^{2+} ions to be reduced by electron flow to the copper metal, forming Cu^0 atoms (nucleation), which then group together (growth) and form nanoparticles in the glaze (figure 2).

These particles are somewhat prevented from growing too large by the kiln heat because large particles are shaken apart back into smaller ones during the firing (I tried this with gold particles of set sizes and found direct trends of them cleaving during firing).[4] However, larger copper particles often form cubes and some few nanocubes were visible in these samples.

As reduction kilns are becoming more and more scarce and technology is invading the ceramics world, people have looked for other ways to get reduction-like effects. Silicon carbide has found its place in ceramics—and not just for constant carbon dioxide (CO_2) production during firing for lava glazes. Several individuals have used silicon carbide (SiC) for reduction effects in oxidation firings—and explicitly for copper reds in oxidation firings, including John Britt, William Chau, and my group at the University of Richmond.

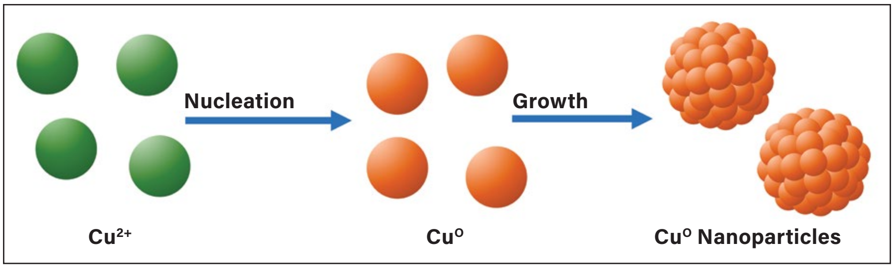

Figure 2: Proposed copper nanoparticle formation during a firing. Note that a 2-electron reduction takes place from Cu^{2+} to Cu^0.

A thermal degradation product of silicon carbide is also CO—carbon monoxide—the same reducing agent that is produced in high-fire gas kilns. This likely abstracts oxygen from the glaze or a local metal pigment, leaves electrons behind, and exits the system as CO_2. Problematically, this is only happening inside the glaze layer, whereas the surface is constantly re-oxidizing from the nature of the firing. As such, only deeper portions of the glaze are reduced, as seen in figure 3. Consistent with procedures for nanoparticle synthesis, the available reductant (electron source) amount would dictate nanoparticle formation and growth. Using this information, a glaze base was made that would support a copper-red nanoparticle growth in a regular cone-6 oxidation firing.

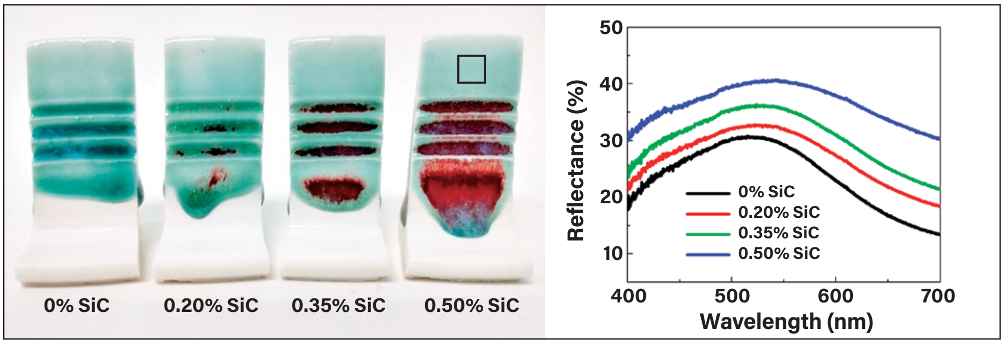

Figure 3: The Poppyfield Glaze base with increased silicon carbide content, left, and reflectance spectra of the top portion of each tile (from black square area), shown right.

Silicon carbide content was increased from 0–0.50% in the glaze, explicitly showing copper-red formation with increased silicon-carbide content. As a cautionary note, silicon-carbide content much above 0.50% results in undesirable glaze frothing caused by excess outgassing and the glaze being unable to seal back over during the firing.

Noticeable in figure 3, left, the green/teal color intensity decreases with increased silicon carbide, which would be consistent with copper (Cu^{2+}) ions being consumed to form copper nanoparticles, which means that there is less copper available for green crystal field color. This is supported by an increased total reflectance (lighter color and more net reflected light) across samples as silicon carbide is added—up to 0.50%.

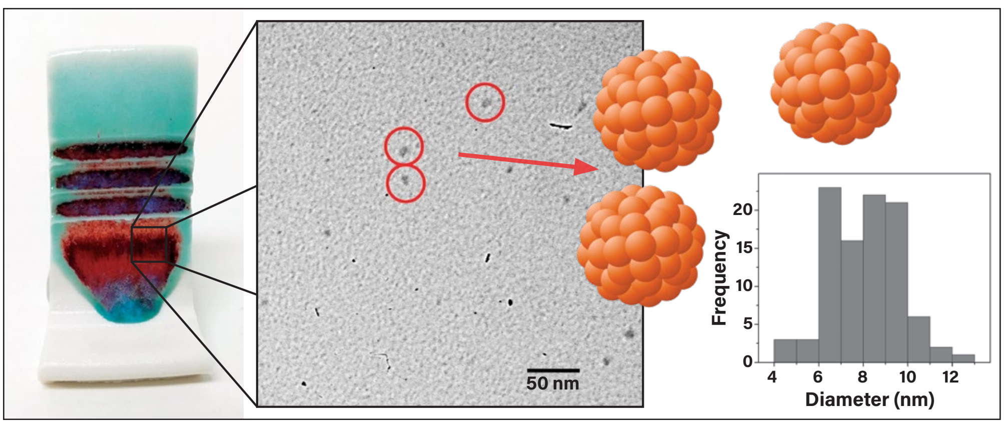

Figure 4: TEM imaging (middle) of a sample of copper red glaze, grown in cone 6 oxidation, left. Nanoparticles were found to be 8.1 ± 1.6 nm with a size distribution shown via histogram (right), but some larger copper nanocubes were also observed occasionally in imaging.

As mentioned previously, the red portions of the glaze are not cuprite (Cu_2O), but sub-microscopic copper nanoparticles that interact with light to make incredibly bright colors. Samples were collected off of the 0.50% SiC tile and imaged with a Jeol TEM to obtain the image visible in figure 4. The circled particles in the TEM image would correspond to copper nanoparticles containing only ~30,000 copper atoms as seen in figure 4, whereas most bulk material is comprised of trillions and trillions of atoms. In addition to these nanospheres, some few nanocubes were observed at ~80 nm diameter, in figure 5. While these were less numerous, a complex growth system likely exists in the glaze as spheres grow into cubes during the firing. A study exploring this is currently underway.

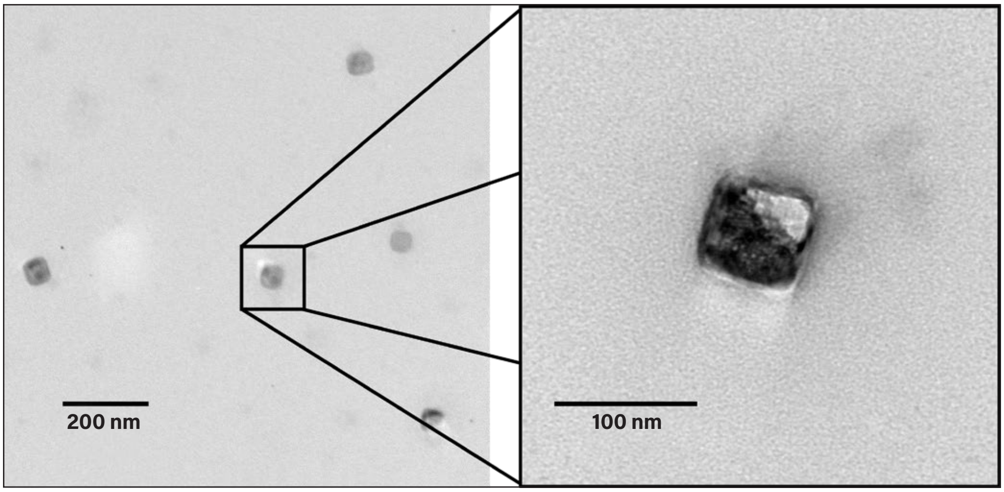

Figure 5: TEM imaging of copper nanocubes (~80 nm) observed in a copper red glaze fired to cone 6 in oxidation.

With copper nanoparticles suspended in the glaze, some really interesting quantum physics can now take place. A phenomenon called surface plasmon resonance (SPR) is responsible for the brilliant color in copper reds. Simply put, natural (or even unnatural, if you're indoors) light strikes the surface of a particle and causes the electrons on that surface to move as a function of that light. These electrons move around to the other side of the particle, creating an imbalance of charge, and then correct back toward the less populated side—resulting in oscillation of electrons around the particle (figure 6, left). The distance that the electrons move and oscillate—contingent on the diameter of the particle—dictates the wavelength of light that is absorbed and the ultimate color of the material by net reflected light, figure 6, right.

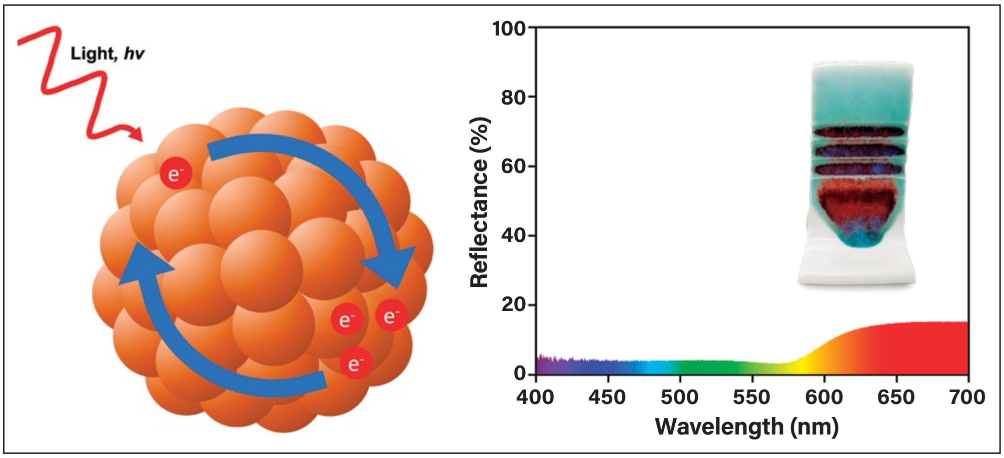

Figure 6: A surface plasmon resonance phenomenon, left, with the resulting color of the glaze after light absorption, right.

As such, an incredibly efficient color system has been hiding in ceramics—but also one that is incredibly fickle. If the particles grow too large, the red becomes muddy and dull. If too small, the red is not sharp and vibrant. If significantly too large, they lose all color properties altogether and the glaze goes clear with a mild green tint—as many of us have seen on our pots glazed with copper reds. Due to this known fickleness, most potters who fire gas kilns for copper reds have precise and dialed-in firing schedules with light reduction ramps and an oxidation cycle at the very end of the firing.

As technology continues to permeate ceramics, and potters let their intellectual curiosity run rampant, we can expect to see more color systems that were previously only possible with reduction firing 20 years ago become everyday standards that are also accessible to those of us with electric kilns and firing at mid-range temperatures.

POPPYFIELD GLAZE
Cone 6 Oxidation

	Gerstley Borate	20.6 %
	Whiting	19.6
	Nepheline Syenite	15.7
	EPK Kaolin	10.8
	Silica	33.3
		100.0 %
Add:	Copper Carbonate	1.5 %
	Tin Oxide	1.0 %
	Silicon Carbide	0.5 %

Fire to cone 6 with a medium ramp schedule. I find that it is best to set a 15-minute hold to allow some of the pinholing to close off from the off-gassed CO_2 that is released as silicon carbide undergoes thermal decomposition and grows your red areas. Note that the red nanoparticle blooms will form in deep places on the clay surface, as they are most protected from surface oxidation and destruction of the copper nanoparticles. This can be taken advantage of by texturing the surface—or intentionally creating deep channels for the blooms to grow in during firing.

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What It All Means

While most ceramic glazes achieve color through crystal field theory, copper reds work through an entirely different mechanism—and do so with noticeably less material than other intense color profiles. Have you ever noticed how a sharp red (in reduction) takes 1.2–1.5% copper carbonate (Pete's Red, etc), but an equally deep green takes 9.3% copper carbonate for Rob's Green?

Nanoparticle color has been shown to be incredibly material-cost efficient, often requiring magnitudes less actual colorant than bulk pigments require for the same color intensities. And while it is somewhat of a different technology and is only recently being explored, it has been happening for millennia, whether we knew it or not.

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1. Ryan Coppage. "Reduction Misnomer." *Ceramics Monthly.* 2016, March 1, 58–59.

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