

Interaction between Cr-bearing pigments and transparent glaze: A transmission electron microscopy study



Louisiane Verger^{a,b,*}, Olivier Dargaud^b, Nicolas Menguy^a, David Troadec^c, Laurent Cormier^{a,*}

^a Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne Universités, UPMC Univ Paris 06, CNRS UMR 7590, Museum National d'Histoire Naturelle, IRD UMR 206, 4 place Jussieu, F-75005 Paris, France

^b Cité de la céramique - Sèvres et Limoges, 2 Place de la Manufacture, 92310 Sèvres, France

^c Institut d'électronique de microélectronique et de nanotechnologie (IEMN), UMR CNRS 8520, ISEN Department, 59046 Lille, France

ARTICLE INFO

Article history:

Received 29 November 2016

Received in revised form 4 January 2017

Accepted 6 January 2017

Available online 18 January 2017

Keywords:

Electron microscopy

Pigments

Glaze

Color alteration

Chromium oxides

ABSTRACT

Spinel ZnAl_2O_4 and corundum Al_2O_3 doped with chromium are used as pink pigments in porcelain glazes. However, alteration of the color can occur during firing, and the resulting glaze appears brown and green respectively, instead of the expected pink. To investigate the mechanism of color change, electron transparent sections were prepared by Focused Ion Beam (FIB) at the interface between pigment and glaze. Observations under a transmission electron microscope (TEM) reveal a common mechanism for both systems. Al migration from the pigment towards the silicate melt results in alteration of the grain of pigments, and formation of a Cr enriched phase, with the same crystalline structure than the initial pigment. Furthermore, the formation of anorthite is reported, due to the increase of the local concentration of Al in the melt. The different morphologies of altered grains of pigment encountered in the glaze are discussed base on the TEM observations.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The stability of chromium-bearing crystals in glasses, slags or melts has been the subject of several studies. The dissolution/crystallization behavior is an important process to understand aggressive attack of refractory materials by molten metallurgical slags and melts [1], crystal/melt partition in igneous processes [2,3] or the possibility of high chromium loading in nuclear glass wastes [4]. Chromium is also used in glaze coatings, painted tiles or porcelain stonewares as sub-microcrystallites that can influence the color or macrocrystallites for aesthetic ornaments (crystalline glazes) [5–7]. Though chromium was isolated only in 1797 by Nicolas Louis Vauquelin in France [8], it was rapidly used to color ceramics, especially at the French Manufacture of Sèvres (Sèvres factory of porcelains) under the leadership of its director Alexandre Brongniart, a former collaborator of Vauquelin [9]. Indeed Cr-bearing crystals produce a richness of colors that was not available before the discovery of this element. A wide range of Cr-bearing pigments was developed yielding to various colorations: pink, red, reddish brown or green [10]. To obtain a glaze, the crystalline pigments are dispersed in an uncolored frit and after firing, the color of the crystal is imparted to the glaze.

The color property strongly depends on the nature of crystal structures incorporating chromium, but it is also altered by possible reactions during firing between the starting pigment and the corrosive silicate melts, i.e. the glazes and frits, as noticed in previous investigations [5–7,11–16]. These works conclude that reactions during firing are most likely due to the dissolution of pigment through chemical attacks. However, the main challenge is still to understand the possible interactions occurring between pigments and ceramic-matrices resulting in a color change after firing.

Previous works were essentially focused on the color change of iron-chromium pigments composed of $(\text{Cr,Fe})_2\text{O}_3$ in zinc-based and zinc-free glazes [6,7,11,12,14]. They reveal the importance of the glass matrix composition, the outward diffusion of Fe into the glaze, and the formation of spinel $(\text{Zn,Fe})(\text{Cr,Fe})_2\text{O}_4$ in zinc-based glazes. For the malayaite pink pigments $(\text{CaSnSiO}_5:\text{Cr})$ used in different glazes, a drastic change of the color also occurs towards paler shades or in the appearance of a bluish hue, attributed to the formation of $\text{BaSnSi}_3\text{O}_9$ [15,17].

At the Sèvres factory, almost 60% of pigments composed of chromium oxides are spinels, synthesized in its laboratory. However, they undergo a change of color in a commonly used uncolored frit. It is a mixture of feldspar, kaolin, quartz and chalk (in proportion specific to Sèvres' porcelain) that vitrifies during the firing process. In this particular decoration, the pink color of spinel and corundum doped with chromium pigments is not stable: the resulting spinel and corundum glazes appear respectively brown and green.

* Corresponding author.

E-mail addresses: louisiane.verger@imcb.cnrs.fr (L. Verger), laurent.cormier@impmc.upmc.fr (L. Cormier).

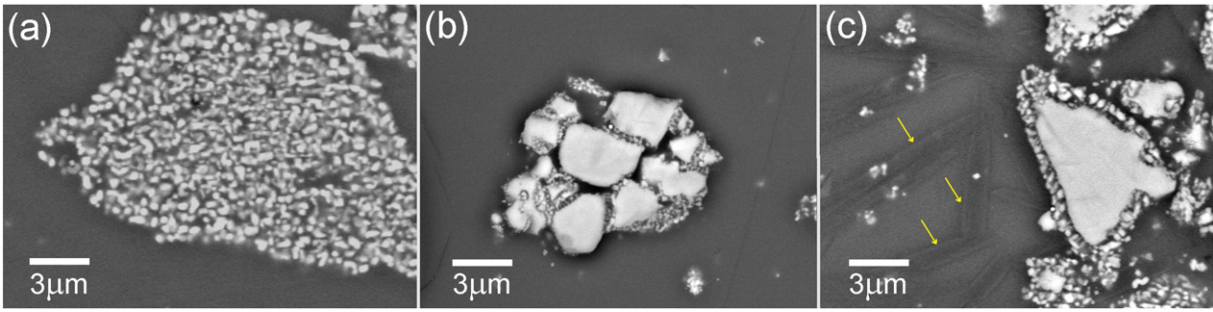


Fig. 1. SEM images of three different grains of pigments in g-spinel glaze, illustrating different reactions of the pigment in the glaze (signal: ASB, EHT = 15 kV): (a) a completely altered grain, composed of spinel-Cr1.46; (b) a partially altered grain, with pristine spinel-Cr0.41 in the center and spinel-Cr1.46 in the periphery; (c) aggregate of partially altered grains with additional phases indicated by arrows.

In our previous investigation on a spinel pigment mainly composed of $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ [16,18], we showed that the color change is caused by a modification of the Cr content in the spinel phase. It was evidenced that the initial pigment $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ gradually dissolves in favor of a Cr-enriched phase $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$.

This behavior is somewhat related to the peraluminosity of the frit/glaze defined as:

$$R = n_{\text{Al}_2\text{O}_3} / (n_{\text{Na}_2\text{O}} + n_{\text{MgO}} + n_{\text{K}_2\text{O}} + n_{\text{CaO}})$$

with $n_{\text{Al}_2\text{O}_3}$ and $(n_{\text{Na}_2\text{O}} + n_{\text{MgO}} + n_{\text{K}_2\text{O}} + n_{\text{CaO}})$ the molar content in alumina and alkali and alkaline-earth oxides in the specimen, respectively. When $R < 1$, the glass is peralkaline and when $R > 1$, the glass is peraluminous. The starting frit has a low peraluminosity of 0.50.

When Al_2O_3 content is increased in the uncolored frit, i.e. the peraluminosity increases, the dissolution of the pigment was found to be reduced. It was concluded that the enrichment in Cr of the spinel after firing results from the gradual migration of Al from the pigment to the glaze, without changing the nature of the crystalline phase.

The color change occurring with corundum doped with chromium pigment was also observed by Martos et al. [5] It was found that the presence of ZnO was required for stabilizing the pink coloration in the glaze. However, the mechanism that underlies this change of color is still not known.

In this paper we will examine several examples of interaction between chromium pink pigments and the frit glass matrix. We will focus on the Al diffusion by analyzing the interface between the pigment and the surrounding glass. Focused Ion Beam (FIB) cross-section

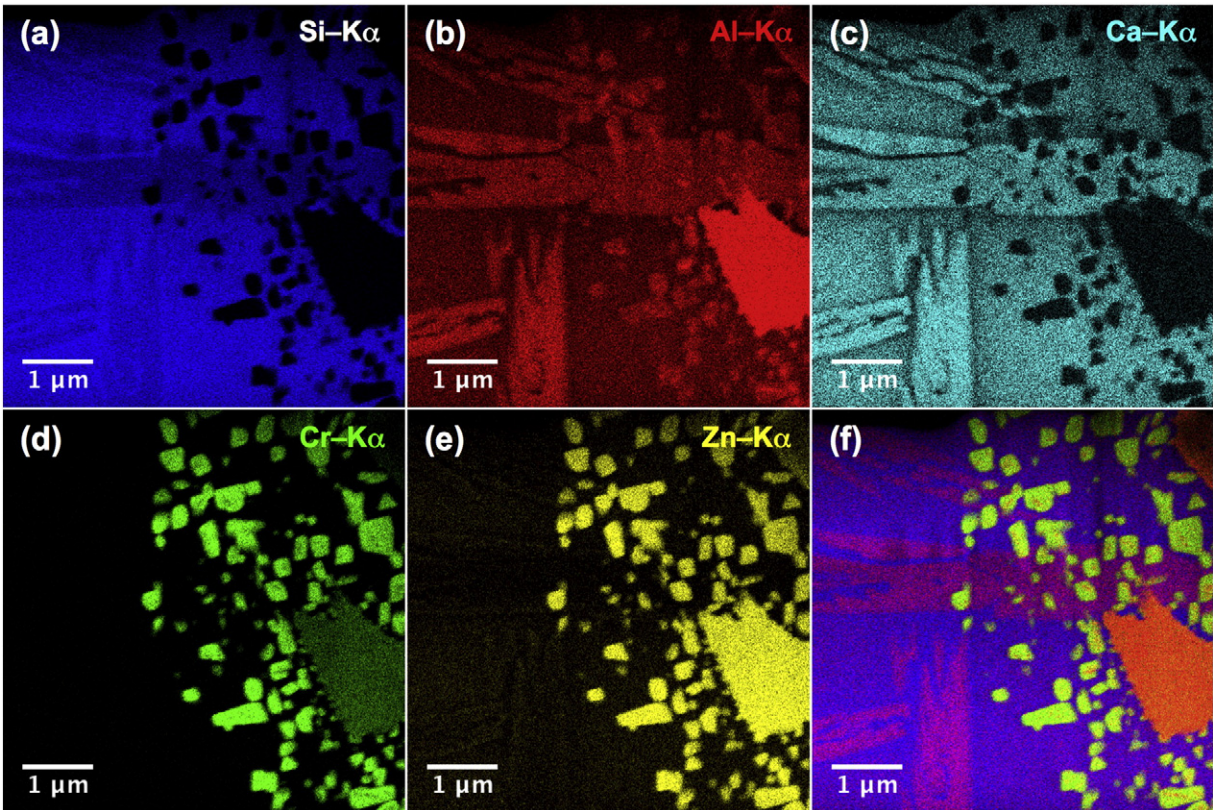


Fig. 2. Elemental XEDS maps of g-spinel sample. (a–e) STEM-XEDS elemental mapping acquired using energy windows related respectively to Si-K α , Al-K α , Ca-K α , Cr-K α , Zn-K α lines. (f) Composite image built with Al, Cr and Si elemental maps. Orange area corresponds to pristine spinel-Cr0.41, bright green areas correspond to Cr-rich spinel crystals, violet areas correspond to a SiO_2 -rich glass and magenta regions are related to an anorthite phase. Elemental maps are not quantitative (not background corrected).

Download English Version:

<https://daneshyari.com/en/article/5441450>

Download Persian Version:

<https://daneshyari.com/article/5441450>

[Daneshyari.com](https://daneshyari.com)