CERAMIC GLAZES WITH AVENTURINE EFFECT

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ABSTRACT

Aventurine glazes consist of a glassy matrix that contains randomly distributed laminar crystals of high reflectivity. Direct incident light causes these crystals to sparkle, producing a glittering effect that varies with the angle of incident light. These glazes can be obtained with Cr, Cu, Fe and U, by crystallising the metal or the oxide. The effect is obtained by mixing oxides of metallic elements with frits, or with 'raw glazes' based exclusively on crystalline raw materials. During firing, the metallic oxide dissolves to give rise subsequently, in cooling, to the laminar crystals mentioned previously. Some references have been found in the literature on the use of aventurine glazes in artistic ceramic ware. The origin of these glazes dates back to the 17th century.

The present study has been undertaken to establish the formation mechanisms of this type of effect, in order to attempt to adapt these to shorter thermal cycles than those used in artistic ceramics. The effect was analysed of mixing iron and copper oxides with ceramic frits with a view to obtaining aventurine glazes. The metallic oxide content, the frit composition, the thickness of the applied glaze layer, and the thermal cycle were modified. It has been verified that iron yields aventurines in which the sparkles are originated by hematite crystals with a dendritic shape or in hexagonal sheets. Depending on either form of the crystal, the shade of the reflections varies. However, the addition of copper can lead to different effects, such as glazes with an intense green colour, glossy metallised glazes with a blue, silver or golden hue, or metallised glazes with a matt surface and silver hue.

1. INTRODUCTION

Numerous decorative effects are used in artistic ceramics, caused by large-sized crystal devitrifications[1-6], particularly noteworthy being those based on willemite crystals (shaped like stars or rosettes of several millimetres in diameter) and the aventurine glazes. However, some confusion exists regarding the description of this last effect. Most authors[2-7,14-18] describe this as the dispersion of laminar crystals with a high refractive index in a glass with a certain degree of transparency, which reflect light in different directions producing a glittering appearance. Some references have also been located which speak of a 'dispersion of microcrystals that provide a glossy appearance'[8] or of a 'surface gloss with a variable colouring that gives a metallic or iridescent appearance'[9,10]. Other authors have studied crystal formation without describing the surface appearance of the glazes[11-13].

The effect, described as small glitters or sparkles of the glaze, which vary with the angle of incident light, originated in 17th century Venice, when copper filings were accidentally spilled on molten glass, with such a surprising effect that it became part of factory production. In fact, the name 'aventurine' comes from the Italian *a ventura*, which means 'by chance'. Later, the same name was used to designate a mineral consisting of quartz with mica inclusions, whose sheets provide it with a glittering effect when the angle of incident light is varied.

A literature survey showed that the elements capable of crystallising as a metal or oxide, to provide the aventurine effect are Fe, Cr, Cu, Ni, Mn and U. Very little systematic information is available on the compositions and the conditions for obtaining these glazes, and no references have been found on the formation mechanisms. The optimum metal oxide content varies for each type of composition. If this is low it dissolves in the glass and does not produce the effect, whereas if it is excessive, large crystals can form in the surface and produce a metallic appearance instead of the sought-after effect[6].

Some references have been found to compositions for iron aventurine glazes[3-5,14,15]. In general, the Fe_2O_3 contents range from 10 to 30% by weight, and there are two groups of glazes, lead and boric, since a molten phase with low viscosity is required for laminar crystal growth. The alumina content must be low and the proportion of SiO_2 is adjusted to obtain appropriate viscosity, as a function of the cycle used to produce the glaze. The glazes can be obtained from glaze compositions consisting of natural raw materials or mixtures of frits and natural raw materials. The Fe_2O_3 may be part of the frit or not, although in most compositions it is directly mixed into glaze, owing to the disadvantages of synthesising coloured frits and because crystallisation occurs more easily than if a homogeneous glass is used[16]. In regard to the aventurines with the other metallic oxides, the only references found have been qualitative: the quantity of metallic oxide varies highly with the composition and is usually introduced by mixing this into the glaze slip composition not in the frit.

The thermal cycle used to obtain these glazes usually consists of two stages: a first one for dissolving the metallic oxide in the melt, followed by slow controlled cooling that allows the laminar crystals to form or, otherwise, a certain dwell time at a lower temperature, where the crystalline growth rate is high. Cycle duration is very long, from 7-8 hours[17] to 24 hours[18].

The formation mechanism has not been described in depth. The copper aventurines develop by Cu^0 crystallisation and need a reducing agent that can be introduced in the glaze[11,13], or it may be the own kiln atmosphere. The complexity of the system explains why, despite being the element with which the first aventurines were obtained, it has not been deeply studied. In the Cr aventurines, hexagonal crystals of Cr_2O_3, fuchsite[8,12], form; in the iron aventurines, hematites crystallise [17,18] or mixtures of hematite and fayalite crystallise[15]. In any case, the dissolution-crystallisation of the oxide or of the metal responsible for the effect involves redox reactions, whose equilibrium depends strongly on the temperature and composition of the melt[19], which is why bubble formation is frequent in the glaze when the starting composition is not balanced.

The present study has been undertaken to establish the formation mechanisms for the aventurine effect, understood as the scattering of crystals absorbed in a non-opaque glass, which produce small sparkles or glitters by incident light, in order to try to adapt the glazes that give rise to this effect to shorter thermal cycles than those used in fabricating artistic ceramic wares.

2. EXPERIMENTAL

Based on the literature surveyed, we started with a frit composition that contained 19% Fe_2O_3 by weight, which was representative of a group of frits that developed the iron aventurine effect. After verifying that the frit produced glazes with an aventurine effect, an iron-free frit was prepared with a view to obtaining the effect with glaze compositions that contained mixtures of this frit with iron oxide. The composition of this base frit, referenced A1, is detailed in Table 1.

OXIDE	SiO_2	Al_2O_3	B_2O_3	Na_2O	BaO
%	65.9	0.7	22.2	10.0	1.2

Table 1. Composition of frit A1 (mol %).

Frit A1 was obtained by fusion at 1550ºC, heating at 10ºC/min. with a 30 min. dwell at this temperature.

Glaze suspensions were prepared from frit A1 with different quantities of hematites, and applied onto fired bodies. After verifying that the sought-after effect had been obtained with one of the tested quantities, we prepared suspensions with 20% hematites, 80% frit, and a 6% kaolin addition relative to the mixture of frit and hematites (percentages by weight), as well as sodium tripolyphosphate and sodium carboxymethylcellulose as additives. These suspensions were applied onto previously fired ceramic bodies to obtain the glazes. The thermal cycles used to obtain the glazes are set out below in the corresponding results section. The resulting glazes were characterised by optical microscopy (OM) and scanning electron microscopy (SEM).

In order to study the dissolution kinetics of the hematites, introduced as raw materials into the glaze composition, the suspension was put into a number of porcelain crucibles, and a series of experiments was conducted. When these mixtures had been dried, the crucibles were subjected to the heat treatment established for each experiment, and subsequently withdrawn from the kiln at the desired temperature to freeze the system. Once at ambient temperature, the resulting glass was separated from the crucible with a disk cutter.

The synthesised glass samples were milled in a ring mill and the crystalline phases present were analysed by means of X-ray diffraction (XRD). The quantity of hematite was estimated by taking the signal corresponding to the most intense hematite peak in the unfired glaze as a reference.

In order to determine the influence of the frit composition on the resulting aventurine effect, a glaze containing a different frit, with high boron content and low melt viscosity, was prepared. This frit was then used to perform the same experiments in the crucibles as those described previously, to study hematite dissolution in the melt.

In order to establish whether the mechanisms found were common to other types of aventurines, glazes were prepared by mixing the tested frits with CuO. The resulting suspensions were applied onto ceramic bodies and fired with different thermal cycles to attempt to obtain the aventurine effect. The glazes obtained were characterised by optical microscopy (OM), scanning electron microscopy (SEM) with an energy-dispersive microanalysis unit (EDX) and X-ray diffraction (XRD).

3. RESULTS

3.1. IRON AVENTURINES. EFFECT OF GLAZE HEMATITE CONTENT

The literature on the aventurine effect mentions very wide ranges of hematite quantities. Therefore, we first determined the most appropriate quantity of Fe_2O_3 for obtaining the aventurine effect with frit A1. For this, glazes were prepared with hematite/frit ratios of 5/95, 10/90, 15/85 and 20/80 (ratios by weight), and the pieces onto which these were applied underwent the following heat treatments:

- Hematite dissolution step in the range [1180ºC, 1200ºC], with dwell times between 6 and 30 minutes.
- Hematite crystallisation step in the range [950ºC, 1050ºC], with a two hour dwell time at this temperature.

The tests conducted indicate that the characteristics of the glaze obtained depended mainly on the quantity of iron in the glaze, as shown in Table 2.

Fe_2O_3 %	APPEARANCE OF THE GLAZE	BUBBLES	CRYSTALS
5	Homogeneous transparent green	Very small and numerous	non-existent
10	Homogeneous very dark reddish colour	Large and numerous	non-existent
15	Very heterogeneous different shades of brown	Large and infrequent	Some are detected in particular points
20	Homogeneous reddish brown	non-existent	Abundant, with aventurine effect

Table 2. Characteristics of the glazes obtained.

The results indicate that a 20% hematite quantity is needed to obtain a glaze without defects and, in addition, that the aventurine effect can be generated. Therefore, the remaining tests were conducted with the highest tested quantity. It may be noted that the presence of bubbles in the glaze seems to be related to the initial hematite content and must be a consequence of the Fe^{2+}/Fe^{3+} equilibrium in the melt.

3.2. HEMATITE DISSOLUTION

The first requirement to obtain an aventurine glaze is that the crystalline phase should dissolve in the glass, so that it can crystallise during cooling in the form of large-sized laminar crystals. Hematite solubility in the frit was therefore studied.

First, we analysed the hematite quantity that dissolved in the A1 frit during the heating step in the glaze with 20% hematite by weight. The crucibles with dry glaze were subjected to heating at 25ºC/min. up to different peak temperatures, and withdrawn from the kiln once these temperatures were reached. Resulting glass appearance differed greatly, depending on the peak temperature (Figure 1). Generally speaking, raising the peak temperature increased glaze flowability, generating a greater volume of gases in the glass and changing the colour from red to blackish.

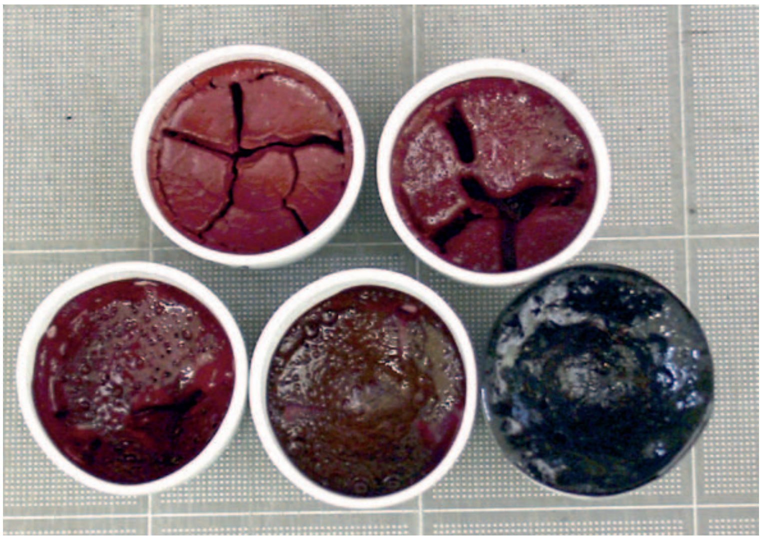

Figure 1. Glaze 80%A1+20% Fe_2O_3 subjected to different heat treatments.

The XRD analysis results show that in all the samples the only crystalline phase present is hematite, whose quantity diminishes notably as peak temperature increases, following a roughly linear tendency as Figure 2 shows. At 800ºC hardly any hematites dissolve, but when the temperature rises, the dissolution intensifies, although it is never complete in the explored range, as at 1200ºC a considerable quantity is still left.

Gas genesis in the glass can be attributed to the Fe^{2+}/Fe^{3+} redox equilibrium, which shifts towards the more reduced term as temperature rises, causing oxygen to form which, once the glass is saturated, will tend to nucleate in the form of bubbles. Since the rise in temperature is accompanied by a rise in dissolved hematite content, the amount of oxygen generated also increases; for this reason, in the crucible treated at 1200ºC, the melt flowed over the brim of the crucible.

In order to determine maximum hematite solubility in the glass, tests were conducted extending the dwell time at 1200ºC to 60 minutes. XRD analysis of the resulting samples (Figure 3) indicates that with a 60 min. dwell, the quantity of undissolved hematite in the glass decreases to 4%, as opposed to 8.5 % when the heating ends at this temperature. It was verified that at a 15 min. dwell, an important quantity had already dissolved.

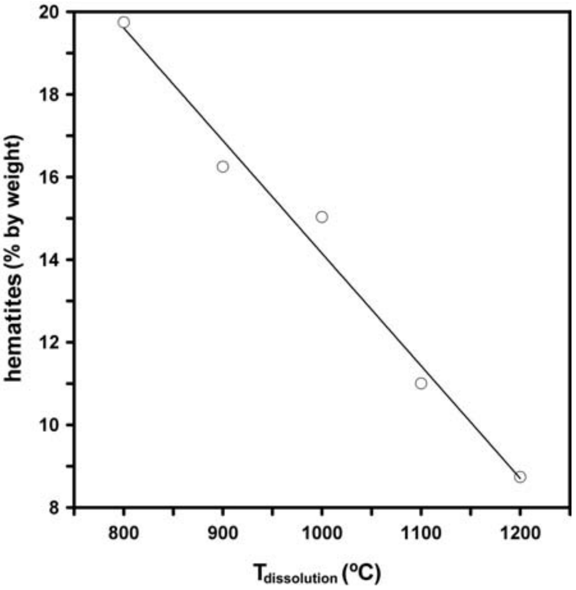

Figure 2. Evolution of the undissolved Fe_2O_3 fraction versus peak heat-treatment temperature.

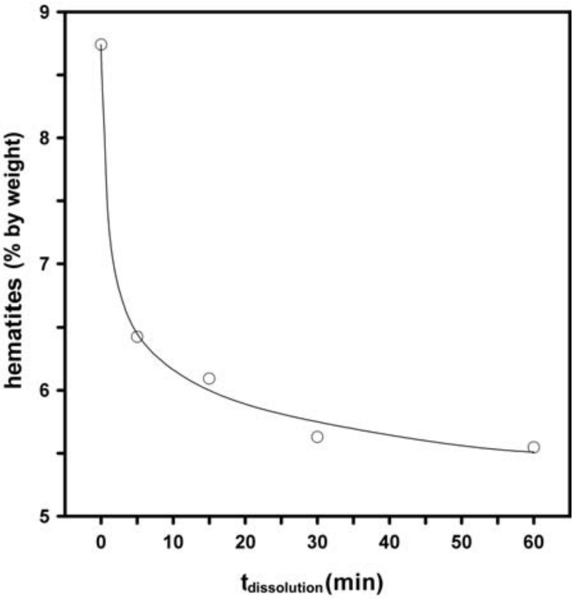

Figure 3. Evolution of the undissolved Fe_2O_3 fraction versus dwell time at 1200ºC.

3.3. HEMATITE CRYSTALLISATION

The hematite crystallisation tests were conducted after a 15 min. glaze dwell at 1200ºC, applying a 2 hour heat treatment at the selected crystallisation temperature.

The XRD results show that the devitrified hematite fraction is very small at temperatures around 1200ºC (Figure 4), but that when the crystallisation temperature decreases, this fraction increases, peaking at a temperature of 950ºC, below which the devitrified fraction of Fe_2O_3 decreases. This behaviour is consistent with the classic theory of crystallisation, since reducing temperature raises the tendency to devitrify, while simultaneously reducing the mobility of the crystal components, as a result of which the crystalline phase fraction maximises at a certain temperature.

In order to obtain the aventurine effect, it is not only important for the hematites to devitrify, but these must also form laminar crystals of a sufficient size to produce intense reflections when they are illuminated at the appropriate angle. For this the habit and size of the crystals present in the glazes obtained were analysed by OM and SEM; this allowed drawing the following relations between the microstructure of the glazes and the thermal cycle in which these glazes had been obtained.

- Crystallisation takes place inside the glass, since practically no crystals are present at the surface. The few crystals present at the surface are partly submerged in the glass, so that they could have nucleated beneath the surface (Figure 5).
- Two types of clearly differentiated crystalline habits are observed, which appear in different regions of the glass. There are crystals with an irregular habit from the partly dissolved initial hematites, and other laminar ones with a hexagonal habit, which correspond to devitrified crystals, although the shape of these crystals is distorted at higher crystallisation temperatures.
- The laminar crystals reach a maximum size exceeding 40 microns at a crystallisation temperature of 1000ºC (Figure 6). At higher or lower crystallisation temperatures, the crystals are smaller, and the most characteristic feature is the appearance of dendritic growth at the crystallisation temperature of 950ºC (Figure 7). In contrast, the size of the smaller, irregular crystals does not appear to change appreciably across the entire crystallisation temperature range. The literature consulted (20) indicates that dendritic growth occurs when the crystal growth rate is very high and melt viscosity is moderate. At lower viscosities, the crystals that form take on a regular habit.

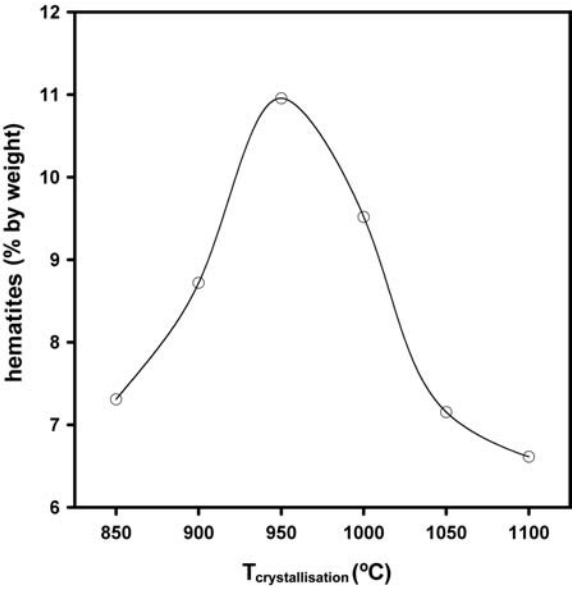

Figure 4. Hematite fraction present in the glaze, after crystallisation treatment.

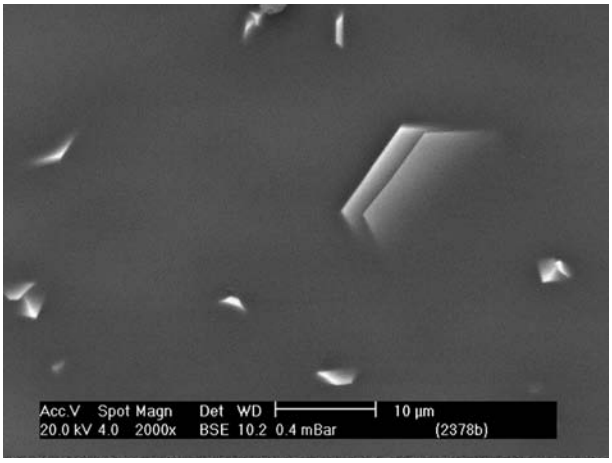

Figure 5. Surface of the glaze after crystallisation treatment at 1050°C.

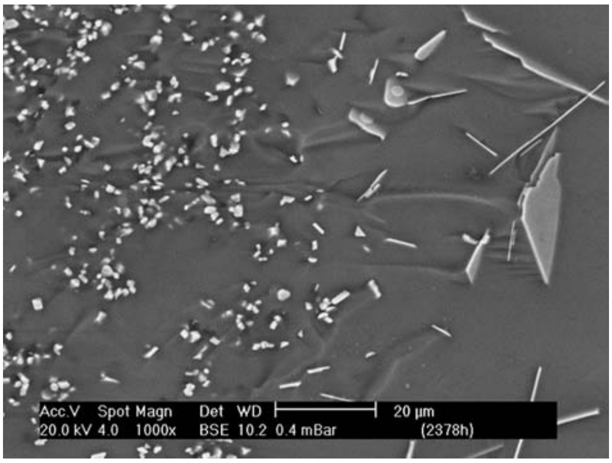

Figure 6. Interior of the glaze (fracture) after crystallisation treatment at 1000°C.

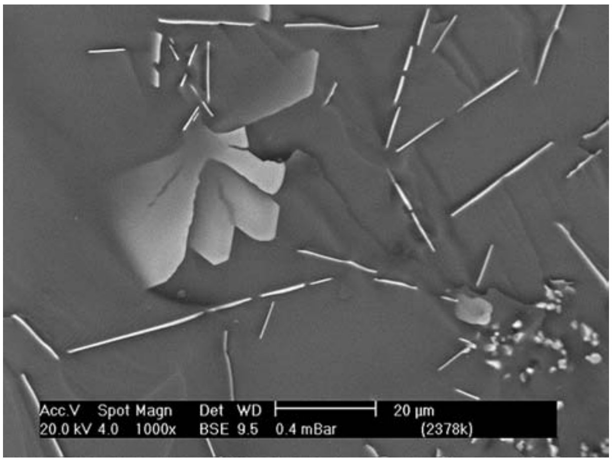

Figure 7. Interior of the glaze (fracture) after crystallisation treatment at 950°C.

3.4. OBTAINMENT OF THE AVENTURINE EFFECT IN GLAZES WITH IRON

The results set out above defined the starting conditions for obtaining glazes with an aventurine effect from the glaze composition formulated with the A1 frit:

a 15 min. dissolution step at 1200ºC and a crystallisation step with a 2 hour dwell at the crystallisation temperature. In this basic cycle we studied the influence of dissolution temperature, dwell time at this temperature, and crystallisation temperature on the appearance of the resulting glazes. This yielded the following findings:

- The effect of crystallisation temperature on glaze appearance is very pronounced in the range between 950ºC and 1100ºC. In the first place, the high quantity of crystals devitrifying at temperatures between 950ºC and 1000ºC provide the glaze with an aventurine effect, with grey-metallic sparkles and an irregular surface as crystal density is so high that many have reached the surface. At higher crystallisation temperatures the fraction of crystals present is smaller, thus obtaining the sought-after aventurine effect with a golden-reddish glitter. On a microscopic level, the crystals adopt a more hexagonal and less dendritic habit as crystallisation temperature increases, while crystal density decreases (Figures 8 and 9).
- The dissolution temperature also notably influences glaze appearance. In the glazes obtained, when the crystallisation step is kept constant (2 hours at 1050ºC) it is observed that at a dissolution temperature of 1180ºC a cellular structure appears in the glaze, made up of hematite crystals that have not managed to dissolve, and newly formed crystals only appear at the intercell boundaries. In contrast, when the dissolution temperature is 1220ºC (with a dwell limited to 5 minutes to avoid degradation of the body), the greater proportion of dissolved Fe_2O_3 causes a massive crystallisation, which yields a glaze with grey-metallic reflections, partially losing the desired effect. On a microscopic level, more crystals of a dendritic type tend to form as the dissolution temperature rises (Figures 10 and 11).
- The dwell time at the dissolution temperature appears to have a much more limited effect on glaze appearance, since in the tested time range (between 5 and 30 min), no important differences are noted, and no differences are detected on a microscopic level either. These results are consistent with those obtained when studying hematite dissolution (Figure 3).
- The cellular structure observed is related to crystallisation and composition gradients. After polishing the glazed surface, it was verified that the intercell boundaries were the favourable sites for the development of large laminar hematite crystal (Figure 12) and, in addition, the glassy matrix displayed a slight enrichment in Ba and impoverishment in Al. In contrast, smaller devitrified crystals appeared inside the cells together with hematite particles that had not dissolved completely, and in these the glassy matrix was slightly enriched in Al (Figure 13).
- Tests conducted introducing Fe as Fe_3O_4 have demonstrated that the dissolution step is facilitated (a smaller dwell time is required at 1200ºC to obtain the aventurine effect), but that more bubbles are generated, which are eliminated during the crystallisation period when the dwell time is sufficiently long. Consequently, the use of magnetite in the glaze composition enables obtaining glazes with an aventurine effect, reducing the duration of the dissolution step of the cycle.

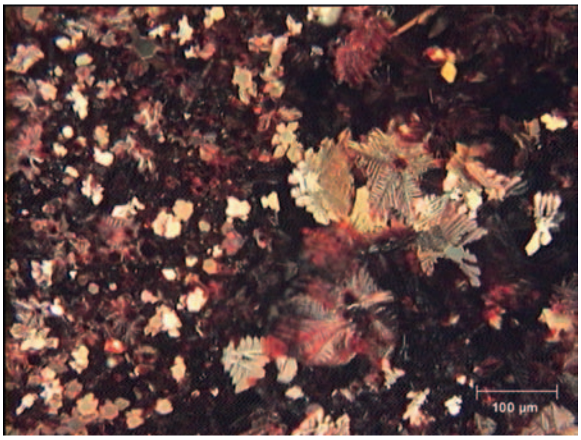

Figure 8. Crystals generated after crystallisation treatment at 950°C (15 min. dissolution at 1200°C).

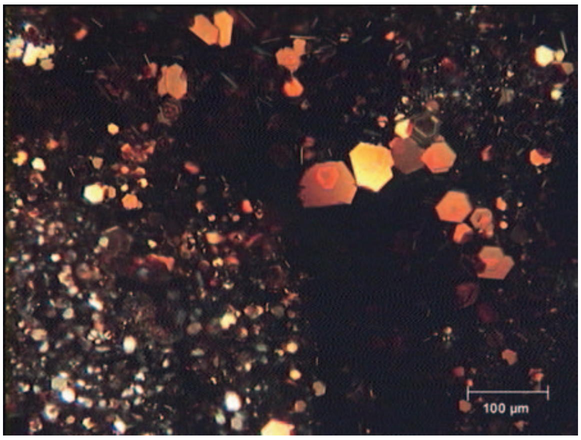

Figure 9. Crystals generated after crystallisation treatment at 1100°C (15 min. dissolution at 1200°C).

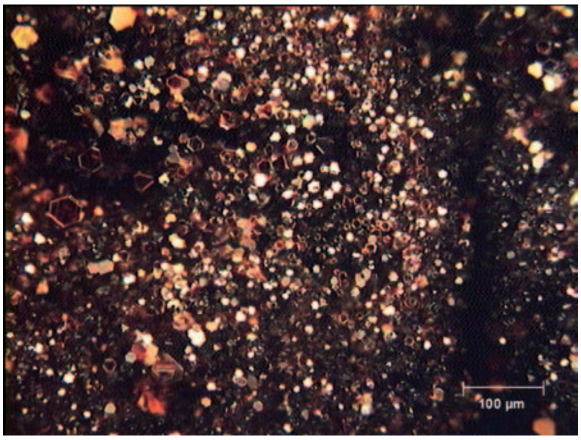

Figure 10. Crystals generated with 15 min. dissolution treatment at 1180°C (2 hour crystallisation at 1050°C).

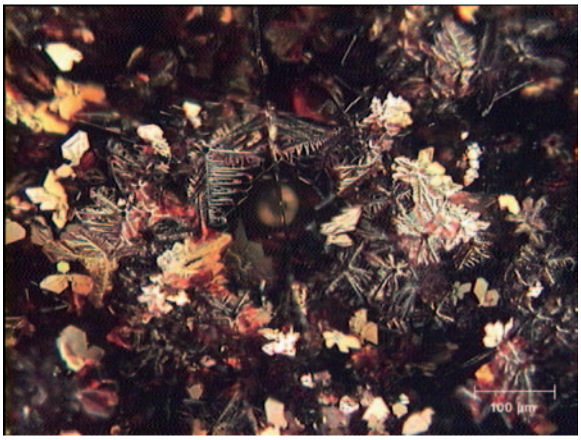

Figure 11. Crystals generated with 5 min. dissolution treatment at 1220°C (2 hour crystallisation at 1050°C).

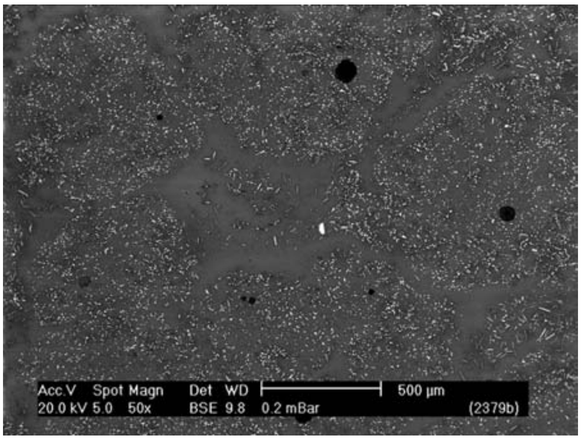

Figure 12. Polished surface of the glaze. Intercell boundary, where large-sized crystals can be observed.

Figure 13. Hematite crystals inside the glaze.

3.5. INFLUENCE OF FRIT COMPOSITION ON THE DEVELOPMENT OF THE AVENTURINE EFFECT IN GLAZES WITH IRON

In order to analyse the influence of frit composition on the development of the aventurine effect in glaze coatings, a glaze composition was prepared mixing Fe_2O_3

with a new frit, A2, which had a composition similar to that of A1. The A2 frit was also very rich in B_2O_3 and Na_2O and contained less SiO_2, which had been replaced with alkaline earths. It was found, first, that the glaze with 20% hematites yielded very opaque glazes, which is why this quantity was considered excessive. The glaze with 15% Fe_2O_3 developed the effect, although a very high tendency towards bubble generation was noted, whose intensity depended on heat treatment.

The hematite dissolution process was then studied in a glaze comprising 85% A2 and 15% Fe_2O_3. It was then observed, in a series of experiments like those described in section 3.2, that Fe_2O_3 dissolved partly in the glass during heating, while magnetite appeared, which dissolved completely when temperatures around 1100ºC were reached, as shown in Figure 14. On the other hand, it was verified that at temperatures below 1100ºC the hematites could be eliminated completely if the glaze was held long enough at constant temperature; however, a quantity of magnetite is reached asymptotically, which does not diminish unless the temperature is raised (Figure 15).

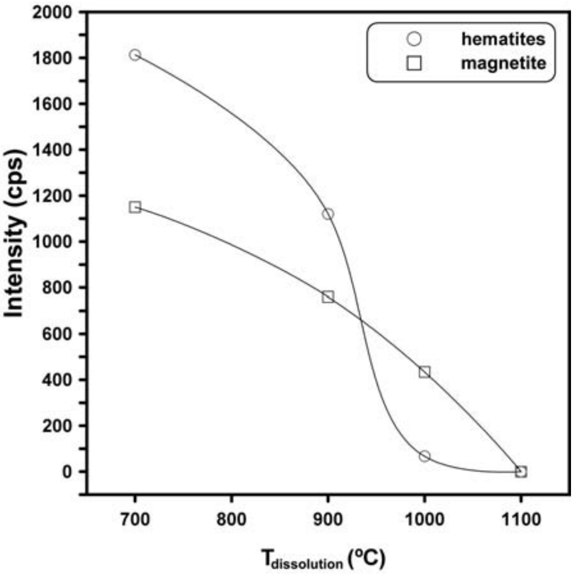

Figure 14. Evolution of the intensity of the two crystalline phases present in the glazes versus peak dissolution temperature.

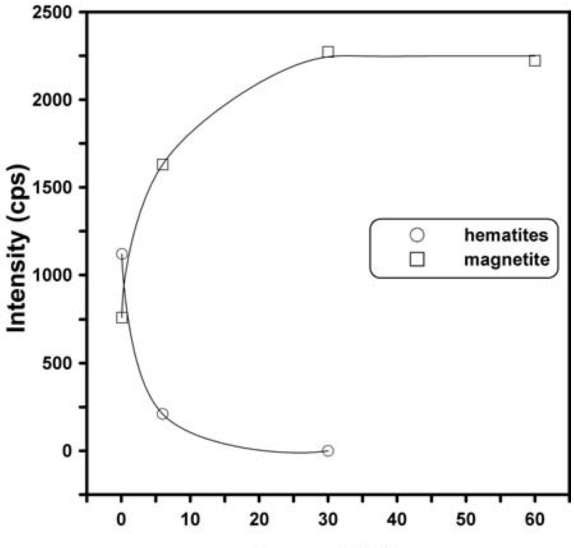

Figure 15. Evolution of the intensity of the two crystalline phases present in the glaze versus dwell time at 900ºC.

Magnetite genesis involves the intervention of the Fe^{3+}/Fe^{2+} redox equilibrium (Equation 1) in the dissolution mechanism, which could be related to the appearance of bubbles that form in the glaze during heat treatment, since magnetite formation involves oxygen release, which can dissolve in the glass until the glass is saturated, which is when bubbles will develop.

$$Fe_2O_3 \leftrightarrow 2FeO + ½O_2 \qquad (1)$$

It can also be interpreted that the arising FeO fraction during heating cannot cause aventurine to form, as this requires FeO oxidation to Fe_2O_3, so that the amount of ferric oxide really available for the devitrification of laminar crystals is less than the theoretically incorporated quantity, consequently leading to a smaller quantity of crystals.

The results indicate that the hematite dissolution mechanism and the appearance of the aventurine effect wholly depend on the composition of the glassy phase. Therefore, a specific study is needed for each frit, to determine whether it is possible to obtain the aventurine effect without defects occurring due to gas generation in the glass.

3.6. OBTAINING THE AVENTURINE EFFECT IN GLAZES WITH COPPER

In order to compare the behaviour of iron and copper oxides on the development of the aventurine effect, glazes were prepared by mixing frit A2 with 15 and 20% CuO, and applying these glaze compositions onto previously fired white bodies. The glazed pieces were fired in an electric laboratory kiln at a heating rate of 25°C/min. to different peak temperatures. The dwell time at peak temperature was 6 min. followed by free cooling in the kiln. The peak temperatures tested ranged from 900 to 1150°C.

It was found that, unlike what occurred with the addition of Fe_2O_3, no bubbles developed in the glazes. The results obtained for both glazes were similar: at maximum temperatures around 900°C the glazes were glossy with a bluish shade; above 950°C they developed a golden shade that went from gloss to matt when the firing temperature was raised. Above 1000°C the glazes were matt with a metallic grey colour, looking very much like matt steel.

When the surface of these last glazes was lightly polished, the metallic appearance disappeared completely, leaving a dark glass, which indicated that a surface effect was involved. In order to obtain more information on this effect, XRD and EDX analysis were conducted of the original as well as of the polished surface of the glaze. It was found that there was CuO in the surface of the glaze. The EDX analysis of the polished surface showed that the interior of the glaze hardly contained any copper. These differences in composition, together with the OM observation of the polished glaze cross-section suggested that a stable separation of immiscible glassy phases took place in the melt and that the Cu was concentrated in the less dense phase. However, since the sought-after aventurine effect was not achieved, both the glazes and the thermal cycles used were discarded.

In some of the consulted references the aventurine effect was associated with the crystallisation of metallic Cu and, consequently, with the presence of some reducing agent [11,13]. On the other hand, it was also mentioned that an excess of the element could produce a metallic appearance[6]. In view of this information, glazes were prepared with frits A1 and A2, with 6% CuO by weight. Metallic Fe was introduced in some of glaze compositions as a reducing agent, while CSi was similarly introduced in others. The glazes were fired according to a two-step thermal cycle; one for CuO dissolution (6 min. at 1100-1150°C) and another one with a relatively long dwell time at a lower temperature to favour crystallisation (60 min. at 950°C). In one of the firings the piece was surrounded by graphite and it was covered with a refractory so that, in addition, firing occurred in a reducing atmosphere. The resulting glazes were green, transparent and glossy, and displayed numerous bubbles, as a result of the redox reactions that had taken place. When the glazed surfaces were observed with the stereoscopic microscope, only some isolated crystals of metallic Cu were detected in the glaze which, using a glaze composition with a reducing agent, had been fired in a reducing atmosphere. These crystals were surrounded by a cloud of bubbles. These results highlight the difficulty of obtaining Cu glazes with an aventurine effect and explain why the little technical information available on this decorative effect is limited to glazes with iron.

4. CONCLUSIONS

In glazes with iron oxide it has been verified that the aventurine effect, involving sparkles or glittering that occurs when light strikes the glaze directly, is due to the formation of large laminar hematite crystals inside the glass, with practically no presence of these crystals in the glazed surface.

The iron oxide content required in the starting glaze depends on how this is introduced, whether as hematites or magnetite, and, particularly, on the composition of the base frit. The degree of saturation in Fe^{3+} needed for hematite devitrification does not just depend on these two variables: heat treatment also plays an important role, possibly related to the rate at which equilibrium is reached in the redox pair Fe^{3+}/Fe^{2+}.

The mechanism involved in producing the aventurine effect in glazes with iron oxides, in which these oxides have been introduced as raw materials in the glaze composition, entails two steps: dissolution in the melt and subsequent hematite crystallisation. In the studied system the maximum crystalline growth rate was found at 950°C, with the devitrification of a large quantity of hematites with dendritic crystals. At slightly higher temperatures (1000°C) the number of arising crystals decreased, while their size increased and their crystalline habit changed, as they became hexagonal sheets. This was beneficial for the decorative effect, since it heightened the intensity of the effect.

The thermal cycle at which the effect with the studied composition was obtained consisted of a dissolution step at 1200°C, with a dwell time of 6 to 15 min., followed by a crystallisation step at 1000°C, with a dwell time of between 1 and 2 hours. The structure and duration of the cycle depend on glaze composition, and need to be fitted to each case.

The aventurine effect in glazes with copper is due to metallic copper precipitation in the melt, which requires a reducing atmosphere; therefore, this was not further pursued.

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