HETEROMORPHIC PIGMENT SYNTHESIS MECHANISMS

G. Monrós, A. García, S. Sorli, M. Llusar, J. Calbo, M.A. Tena

Unit for Environmental Inorganic Chemistry and Ceramic Materials
Dept. Inorganic and Organic Chemistry
Universitat Jaume I, Castellón

ABSTRACT

In the present study, the synthesis mechanisms of encapsulated or heteromorphic pigments are discussed, and the results obtained in the case of coral pink and zirconia-vanadium yellow are set out, when synthesis strategies are used, based on complexing-coprecipitation methods. The control of microstructure by complexing-precipitation methods allows obtaining better results in the first case, in agreement with the proposed mechanism. However, if encapsulating takes place by a phase-transition mechanism, the chemical design of the precursors is not relevant, since the pigment is structured on cooling the system.

1. INTRODUCTION

Heteromorphic pigments are inorganic structures integrated by two phases: a matrix or encapsulating protector phase and the guest phase, which is usually the chromophore. Among the pigments of this nature, particularly noteworthy is the hematite encapsulated in silica, cadmium sulphoselenide encapsulated in zircon, hematite in zircon or coral pink and vanadium yellow in zircon.

In this type of pigments, the chromophore particle is occluded in an encapsulating matrix, which is stable thermally and on exposure to glazes. The occluded chromophore compound and the non-coloured matrix are insoluble, while the solid solution mechanism of the former in the latter is not important, and the size of the occluded particle is sufficiently large (usually colloidal), so that each of these particles is a chromatic unit.

Based on the above, in the encapsulated pigments, the particles responsible for colour are nanometric crystals occluded during the matrix sintering process.

The production of this type of pigments is directly related to the sintering process and/or crystallisation of the matrix, which should be in appropriate synchrony with the nucleación-growth process of the occluded chromophore phase, without the two processes interfering.

In this sense, the control methods of these two stages are fundamental with a view to having the chromophore particle grow in an appropriate way in location and size in the same range of temperatures, so that it can be trapped by the matrix particles in their sintering process.

I) CRYSTALLISATION-SINTERING MECHANISM

V. Lambies and J. Ma. Rincón outline a crystallisation-sintering mechanism for the occlusion of solid solution crystals $Cd(S_xSe_{1-x})$ in a zircon network[1]. The colour of the pigments based on solid solutions of CdS and CdSe hexagonal crystals varies from yellow to dark red depending on the quantity of Se present in the solid solution. These pigments are easily diluted by the glazes and are sensitive to the atmosphere and to calcination temperature, besides involving Se and CdS, which are hazardous materials that require additional measures for occupational health and safety. In 1992, the American OSHA lowered the TWA (Time Weighted Average) limit of Cd in occupational environments from an average of 500 μm/Nm3 in 8 hours to 2 μm/Nm3 although tests were able to indicate the non-bioavailability of Cd from $Cd(S_xSe_{1-x})$.

With a view to improving the colour stability, encapsulating methods in zircon were developed. The encapsulating efficiency is low and the problems of thermal and chemical stability have not been solved completely. They should be managed as hazardous products, both in production and use, since they are sensitive to chemical attack.

The occluded pigment formation mechanism consists of the following stages:

1) Formation of the zircon guest crystals, $Cd(S_xSe_{1-x})$ and liquid phases.

For zircon formation, mineralisation by means of fluorides produces liquid phases that improve reactivity through diffusion and it cannot be stated that it is only due to the formation of SiF_4[5].

The Cd(SxSe1-x) crystals can be obtained previously by coprecipitation on adding a solution of sodium sulphoselenide to a cadmium salt or a suspension of a mixture of an insoluble cadmium salt (carbonate, hydroxide or oxide) and a soluble one (nitrate or sulphate). These crystals can also be produced in situ by reaction of Se with CdS or of the mixture S and Se with $CdCO_3$ at temperatures between 450-600°C.

2) Zircon sintering and occlusion of $Cd(S_xSe_{1-x})$.

The presence of glassy phases of Li_2SiO_3 (Na_2SiO_3 in the case of using NaF as a mineraliser instead of LiF), produces a reordering of the newly formed small-size zircon particles, which grow, according to classic sintering theory, through a dissolution and precipitation mechanism, with surface transport contributing to the interparticle bond. If in the process, one of the small newly formed $Cd(S_xSe_{1-x})$ microcrystals is trapped in the sintering fronts, its effective occlusion takes place according to the sequence shown in Fig. 1. The authors indicate that the occlusion efficiency is low since only the very small $Cd(S_xSe_{1-x})$ crystals are susceptible of being trapped by the zircon grains.

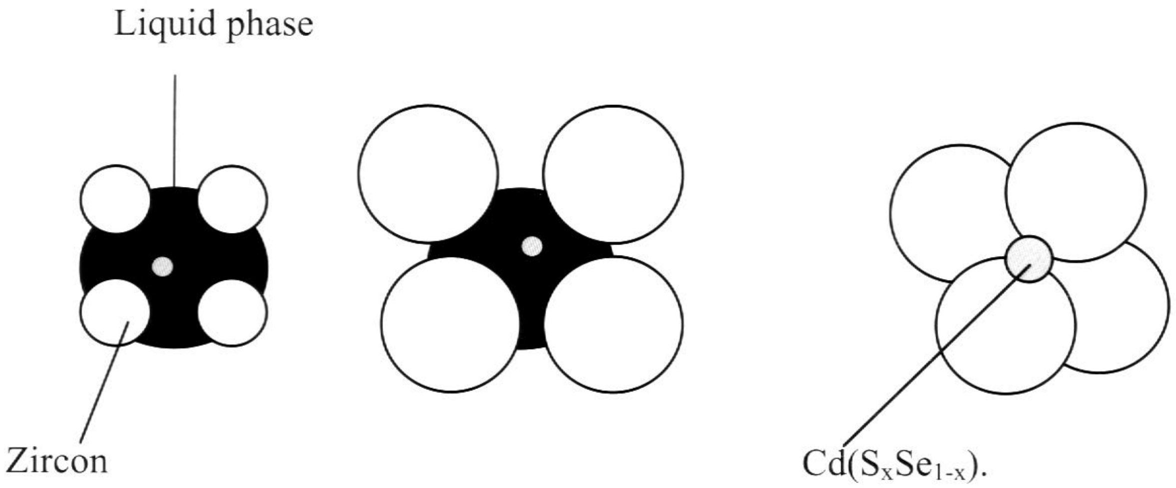


Figure 1: Crystallisation-sintering mechanism.

II) SINTERING-GROWTH MECHANISM

For other such pigments as iron coral in zircon or iron in hematite, the previous mechanism does not seem possible, as the pigment can be obtained from the hematite itself, on choosing the appropriate mineraliser. M. Llusar[3] proposes the reaction sequence in Figure 2 as a general model:

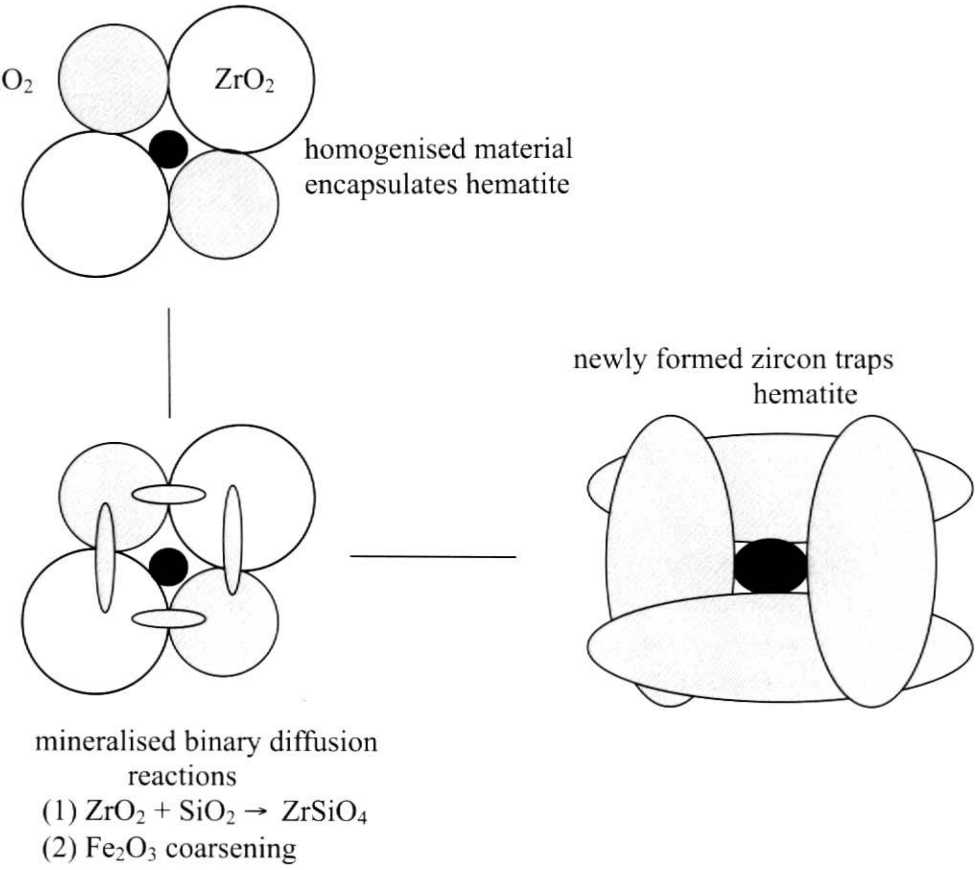


Figure 2. Hematite occlusion in zircon by the diffusion model.

1) Zircon formation in the presence of hematite.

A zirconia particle with a fine hematite particle at its surface reacts with the silica in a binary diffusion mechanism to yield zircon.

2) Sintering of the zircon grains.

The formed grains of zircon sinter with other neighbouring grains encapsulating the hematite particle that remained in its site, although it could grow during the previous process by diffusive growth. If it grows excessively, encapsulation may not be feasible, since synchrony is required between hematite growth and surrounding zircon sintering as indicated in Figure 2.

Adopting this model, the consequences in synthesis are:

(a) quartz or zirconia grain size in an important parameter.

(b) the interaction of iron with silica or with zirconia depends on the mineralising agent, while hematite coarsening also depends on this agent. The mineraliser should facilitate the zircon formation reaction and inhibit hematite growth.

(c) if there is no effective encapsulation, the hematite remains unprotected and colour is not produced; this happens because of elevated temperature, high hematite growth or inappropriate zircon development.

The main difference between this model and the previous one is that in this model, the process of crystal formation (guest and host), sintering and encapsulating, are processes that are considered to run simultaneously. In favour of this model would be the fact, widely confirmed in the literature, that one cannot obtain the pigment from zircon directly mixed with mineralisers and the iron precursor: if the problem only involved some zircon crystals sintering and encapsulating hematite crystals, it should be possible to obtain the pigment from zircon, thus suggesting the simultaneity of the crystallisation-sintering-encapsulating processes. In both cases, the presence of liquid phases generated by the mineralisers is fundamental for developing the diffusion processes involved at high enough rates.

III) PHASE TRANSFORMATION MECHANISM

The vanadium yellow in zirconia is a pigment (DCMA 1-01-4) known from time immemorial. Since the 60s it has lost ground, just as other yellows such as pyrochlore Naples yellow ($Pb_2Sb_2O_7$) or vanadium-cassiterite yellow after the discovery of praseodymium yellow in zircon, which generates more brilliant, cleaner yellows.

Although different authors have affirmed the mordant nature of the pigment[4], others consider it a vanadium solid solution in the monoclinic zirconia network[5]. Cherepanov[6] indicates the importance that the tetragonal→monoclinic transformation of zirconia can have in the synthesis of the pigment; it is necessary to operate at temperatures above 1170°C, the temperature at which zirconia becomes tetragonal zirconia, to produce the pigment.

Studies carried out by G. Monrós[7] in the system $V_yZr_{1-y}O_2$ with $y = 0, 0.04, 0.14, 0.28$ using organic sol-gel methods (zirconium n-propoxide and vanadium(IV oxyacetylacetonate)), aqueous sol-gel (NH_4VO_3 and zirconium acetate) and the conventional ceramic method (zirconia and NH_4VO_3), indicate on calcining from 500 to 1300°C, with holds of 12 hours, that in the gels a crystalline sequence takes place with temperature: glass → tetragonal zirconia → monoclinic zirconia, without producing zirconium pyrovanadate, which is found in the ceramic routes and hydrolysed alkoxide samples. The gel samples exhibit profuse cracking associated with the metastable tetragonal →monoclinic transformation, and displacements are not observed in the significant diffraction peaks, while the yellowest samples also present less surface vanadium measured by EDX. In view of these facts and discussions, the yellow vanadium pigment in zirconia seems to be an occlusion of disaggregated vanadium oxide (V) of the glasses that are generated during calcination. The better disposition of the gel routes to produce these metastable glassy materials explains that they are able to encapsulate more vanadium than the ceramic route, in which the pyrovanadate decomposition generates vanadium pentoxide of relatively large particle size, which is eliminated by volatilisation or washing.

2. OBJECTIVES

The present work sets out the results obtained for coral pink and zirconia-vanadium yellow when synthesis strategies are used based on complexing-coprecipitation methods. The control of microstructure by complexing-precipitation methods in the first case allows obtaining better results in agreement with the proposed mechanism, however in the second case microstructural control is not as important as control in the phase transformation process developed with thermal hysteresis.

3. COMPLEXING-COPRECIPITATION IN IRON ENCAPSULATION IN ZIRCON (CORAL PINK)

A formulation was prepared with classic halogen mineralisation $(SiO_2)(ZrO_2)_{0.97}(NaF)_{0.4}(Na_2SiF_6)_{0.18}(KNO_3)_{0.15}$ (in the BOIAS composition the KNO_3 was eliminated), obtaining the material by non conventional methods of solid chelation-impregnation according to the scheme in Figure 3. Iron sulphate was dissolved in 0.5 M oxalic acid; the precursor solid to be impregnated was added (quartz or zirconia supplied by J.J. Navarrese S.A.) and after 1 hour of impregnation in continuous stirring, it was alkalinised with ammonia until gelling or precipitation of yellow ferrous oxalate. The resulting impregnate was dried and the corresponding mineraliser and precursor added, with dry mixing in a ball mill.

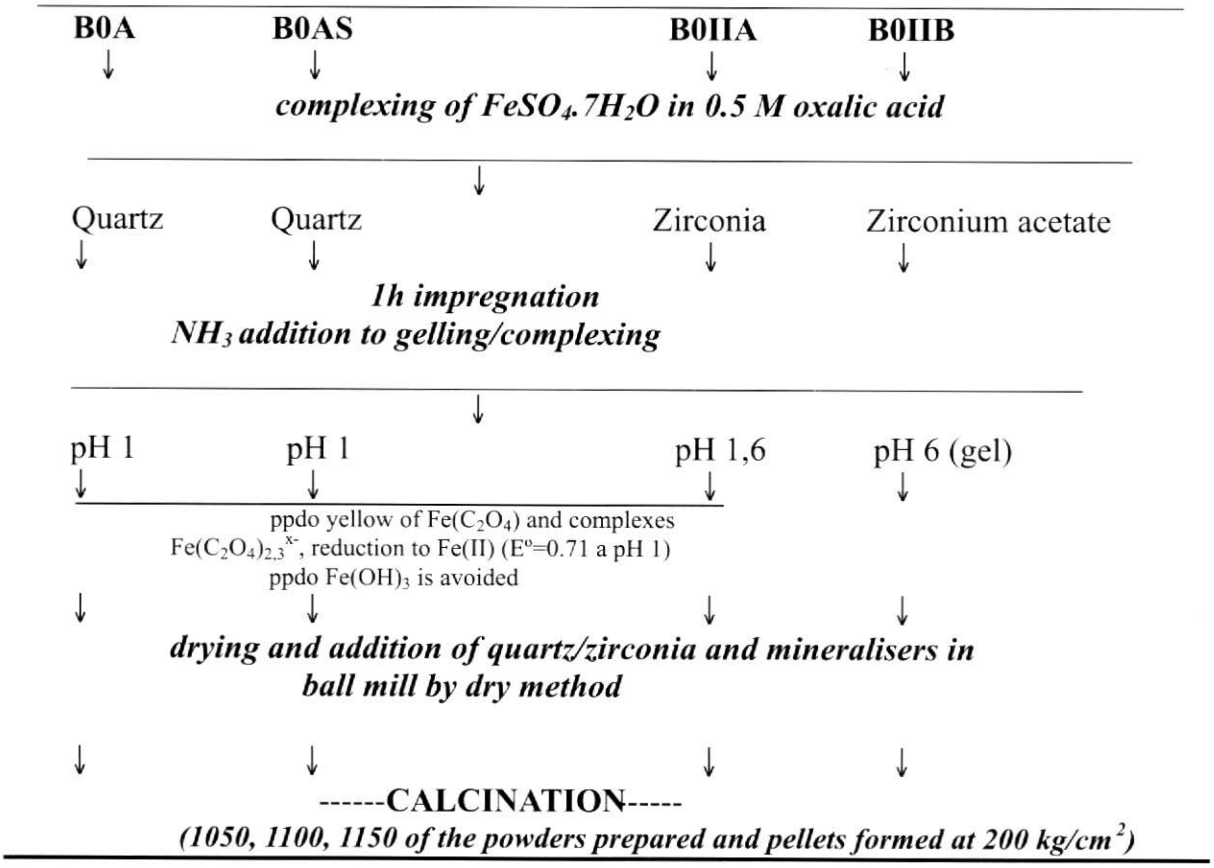


Figure 3. Impregnation samples.

Table I details the results obtained with these samples. The leachings were carried out on powder micronised in a ball mill with 60% water at 800 rpm for 20 minutes: the decantation waters were kept, the powder produced was washed with 50 mL water, stirring the mixture vigorously and collecting the washing waters by decantation. The mixture of micronised waters and washing water was collected and gauged at 100 mL; on these waters Fe(III) was analysed by colorimetry with tiocyanate, and sulphates by gravimetry with barium.

SAMPLE	**1050°C**	**1100°C**	**1150°C**	**1100°C/** Pellet
CERAMIC				
Calcine colour	orange	orange	orange	
Glaze colour L*a*b*	orange 55/27/23	orange 54/27/22	orange 57/22/18	
XRD	Z(950)H(60)	Z(1070)H(70)	Z(1050)H(80)	
mg Fe/Kg	1	1	4	
mg SO_4^{2-}/g	420	416	470	
BOIA				
Calcine colour	orange	orange	light orange	orange
Glaze colour L*a*b*	orange 59/26/25	orange 52/31/24	orange 60/24/24	orange 62/19/19
XRD	Z(1045)H(64)	Z(966)H(69) C(29)	Z(1039)H(59)	Z(669)H(36) M(153)
mg Fe/Kg	13	20	13	600
mg SO_4^{2-}/g	21	20	24	300
BOIAS				
Calcine colour	brown	brown	brown	dark brown
Glaze colour	pink	pink	pink	colourless
XRD	Z(831)H(52)	Z(990)H(59)	Z(925)H(66)	Z(673)H(38) M(176)
mg Fe/Kg	4	6	9	350
mg SO_4^{2-}/g	19	21	24	200
BOIIA				
Calcine colour	orange	orange	orange	brown
Glaze colour L*a*b*	orange 57/28/25	orange 57/25/22	orange 57/22/22	very light orange
XRD	Z(983)H(76) M(20)	Z(1039)H(62)	Z(1212)H(58)	Z(458)H(29) M(181)
mg Fe/Kg	6	8	34	350
mg SO_4^{2-}/g	22	23	23	160
B0IIB				
Calcine colour	grey	grey	grey	grey
Glaze colour	colourless	colourless	colourless	colourless
XRD	Z(861)H(56)	Z(860)H(46)	Z(958)H(54)	Z(363)M(233)
mg Fe/Kg	27	40	-	600
mg SO_4^{2-}/g	42	40	-	128

TABLE I. Impregnation results.

The samples were calcined in an aluminosilicate crucible with manually pressed powder, sealed with quartz.

The data in Table III shows:

(a) The optimum impregnation is that of zirconia (BOIIA sample) with L*a*b*=57-28-25 at 1050°C. However, the impregnation of quartz (BOIA) also produces good results, L*a*b*=59-26-25 at 1050°C and 52-31-24 at 1100°C in the level of the values obtained by means of the ceramic method.

(b) In opposition to the result obtained with the coprecipitates studied by Llusar et al.[3], where the Si-Fe premixes in the coprecipitate yielded orange colours and Zr-Fe premixes did not produce colour, in this case both previous impregnations produce colour.

(c) The zirconium acetate gels do not yield colour, confirming the results detected in gels with a high organic degree (gelatins, citrates and alkoxides) studied by Llusar et al.[3].

(d) The pellets do not develop colour, the relatively better results being found with B0IA. Pressing inhibits zircon reactivity, with a significant decrease in the intensity of its peaks and a considerable increase in those of zirconia being observed in all the samples.

(e) The analytic levels are very low and relatively similar: Fe^{3+} presents values in the range 10-40 mg Fe/kg colour (in pellets this increases to 350-600), while the SO_4^{2-} oscillates in the range 20-40 mg SO_4^{2-}/g colour (in pellets it rises to 150-300). For the iron these values are higher than the ceramic treatment of the sample, however sulphate leaching in the impregnated samples is very low compared to the ceramics. The samples formed into pellets present strong leachates in iron and in sulphates.

4. COMPLEXING-COPRECIPITATION IN ENCAPSULATING VANADIUM PENTOXIDE IN ZIRCONIA

This pigment has usually been investigated by further structural characterisation of the powders, leaving aside its pigmenting and microstructural characteristics on being dispersed in glazes[4,5]. In heteromorphic pigment powders, the free colouring phases almost always appear (hematite, cadmium sulphoselenide, vanadium pentoxide, etc.) and therefore, although the techniques for eliminating inactive free species by washing or melting are adjusted, these powder colouring phases always remain and distort the observations and measurements performed on them. That is to say, an intense red or yellow powder does not ensure that the behaviour in the glazes will also be intense; they may often not even be able to colour the glazes.

The present work has analysed the development of the pigment in monoporosa glazes in terms of three parameters: (I) the vanadium precursor used, (II) use of sol-gel methods and (III) use of vanadium complexing agents as vanadates (Tb_4O_7 and In_2O_3).

4.1. EFFECT OF THE VANADIUM PRECURSOR USED

The composition $0.2V_2O_5.ZrO_2$ was synthesised, using three different vanadium precursors, V_2O_5 supplied by Merck, 99.9% rich, NH_4VO_3 and $VOSO_4$ by PANREAC (analysis grade).

V_2O_5 melts at 690°C and presents a eutectic at this temperature with 20 mol% ZrO_2 in the V_2O_5-ZrO_2 phase diagram. In the studied composition V_2O_5 represents 29 mol% of the mixture. According to the phase diagram, above 690°C liquid phase and zirconium pyrovanadate ZrV_2O_7 coexist up to 760°C, at which pyrovanadate decomposes, leaving a liquid containing around 40 mol% V_2O_5 in equilibrium with zirconia.

Ammonium metavanadate decomposes into V_2O_5 and ammonia around 200°C and the vanadyl sulphate decomposes into vanadium pentoxide above 600°C. The zirconia presents a well-known polymorphism indicated by the multi-equation :

1000-1120°C

Monoclínic → Tetragonal → Cúbic

5,56 g/mL ← 6,10 g/mL 2370°C melting 2680°C [Eq. 1]

IC=7 *930-650°C* *IC=8* *IC=8*

+9%volume

The hepta-coordinate monoclinic crystalline form is the stable form at ambient temperature; at temperatures around 1000°C it begins to transit to the tetragonal form, which like the monoclinic, are distorted fluorite-type forms with coordination number 8 in the tetragonal polymorph; the transition does not conclude below 1120°C and at 2370°C it transits to the cubic form with a fluorite structure. On cooling strong hysteresis takes place in the tetragonal-monoclinic transformation, as it does not begin above 930°C and does not end before 650°C. This type of transition, which develops in a non-thermal and non-adiffusional way, is similar to the martensitic transformation that can be observed on tempering steels, in which austenite (C in FCC iron) metastabilises in martensite (C in BCC iron distorted in the c direction), without producing ferrite (C in BCC iron) and cementite (FeC_3). For this reason, the tetragonal-monoclinic transformation, which raises the toughness of the stabilised material, is also known as the martensitic transformation of zirconia. In this transformation, the monoclinic polymorph, which is less compact than the tetragonal one, on crystallising produces strong shrinkage in the material, which cracks and breaks, this being the reason that zirconia cannot be used as a structural refractory.

It is evident that the formation of the vanadium-zirconia pigment is affected by the form in which vanadium (precursors) enter the reaction as well as the curious and unforeseeable hysteresis in the tetragonal-monoclinic transformation of zirconia. With a view to analysing both effects, samples were prepared with the three precursors mentioned and calcined at 1100°C/2hours (transformation to incomplete tetragonal) and at 1200°C/2hours (completed transformation). The vanadium precursors and monoclinic zirconia supplied by J.J. Navarrese (mean particle size of 3 μm) were mixed in a planetary ball mill with acetone. The calcined powders were micronised in water and repeatedly washed with hot 0.3M HNO_3 to eliminate the non-retained vanadium.

Table II gives the results of the crystalline phases detected by XRD as well as the results of the colorimetric CIEL*a*b * evaluation of the samples glazed at 5% with a conventional monoporosa glaze.

The results listed in Table II indicate that the best yellow-orange colouring obtained with the powders in the monoporosa glaze present CIEL*a*b* values around 80/9/40 on calcining the samples at 1200°C. With the vanadyl sulphate, which produces vanadium pentoxide only after decomposing around 700°C, the level of previous coloration was not produced in any of the repetitions performed. However, with the metavanadate and the vanadium pentoxide obtaining the colorations is not ensured: on numerous occasions the samples at 1200°C did not reach the 80/9/40 colorations, the colour thus exhibiting low reproducibility.

Sample	V Precursor	1100°C/2h	1200°C/2h
V0	V_2O_5	Powder colour: greenish L*a*b*=92/2/23 XRD:M(f)V_3O_5(md)	Powder colour: yellow-orange L*a*b*=84/9/32 XRD:M(mf)
MO	NH_4VO_3	Powder colour: greenish-yellow L*a*b*=87/4/28 XRD:M(f)V_3O_5(md)	Powder colour: yellow-orange L*a*b*=80/9/41 XRD:M(mf)
SO	$VOSO_4$	Powder colour: greenish-yellow L*a*b*=89/-1/25 XRD:M(f)V_3O_5(md)	Powder colour: lemon-yellow L*a*b*=89/-1/25 XRD:M(f)V_3O_5(md)

Table II. Results obtained with the different vanadium precursors by the ceramic route in sample $0.2V_2O_5.ZrO_2$. Peak intensity and crystalline phases detected: md(very weak), d(weak), m(medium), f(strong), mf(very strong), M(monoclinic zirconia).

4.2. USE OF THE SOL-GEL METHODS

When zirconium oxide is produced by precipitation from colloids or salts and zirconium compounds, tetragonal zirconia metastabilises[7]. Tetragonal zirconia crystallises from amorphous gels with nanometric crystallite size and it transforms into monoclinic when the crystallites exceed the critical Garvie size around 30 nm. The Garvie tetragonal-monoclinic transition presents a thermal transformation range that depends on the modifier species present; the presence of vanadium accelerates the transformation[8] while that of praseodymium slows it down[9].

To investigate whether the vanadium zirconia pigment can be obtained in association with the Garvie transformation, gels were prepared of composition $0.2V_2O_5.ZrO_2$ dissolving ammonium metavanadate in concentrated HCl (20 mL for the NH_4VO_3 needed to prepare 5 g of the final product), adding 150 mL water per 20 mL HCl used and dissolving the zirconium precursor used (zirconium acetate supplied by Aldrich, 22.3% rich in ZrO_2). The dissolution thus obtained was gelled by dropwise addition of concentrated solution of ammonia, producing a transparent yellow gel around pH 6. The oven-dried gel was subjected to calcination at 700°C, 1000°C and 1200°C with holds of 2 hours. The resulting powders were micronised in water and repeatedly washed with hot 0.3M HNO_3 to eliminate non-retained vanadium.

Table III sets out the results. It shows that only in the sample calcined at 700°C is it possible to detect the presence of non-transformed tetragonal zirconia. In the three calcinations the zirconium pyrovanadate ZrV_2O_7 has recrystallised on cooling as predicted by the V_2O_5-ZrO_2 phase diagram. However, this recrystallisation of the pyrovanadate was not observed in the ceramic samples. Under the working conditions used, it was not possible to produce the yellow orange colour obtained by the ceramic routes; this is indicated by the reiteration in sample preparation. Pyrovanadate recrystallisation is considered the cause of this impossibility.

T(°C)	Washed colour powder	XRD	CIEL*a*b*
700	Verde	M(mf)T(md) ZrV_2O_7(d)	90/-4/-4 (greenish)
1000	Verde	M(m) ZrV_2O_7(d)	92/-4/10 (greenish-yellow)
1200	Yellow	M(m) ZrV_2O_7(d)	87/-4/30 (lemon-yellow)

Table III. Results found with gels $0.2V_2O_5.ZrO_2$. Peak intensity and crystalline phases detected: md(very weak), d(weak), m(medium), f(strong), mf(very strong), M(monoclinic zirconia), T(tetragonal zirconia).

4.3. USE OF VANADIUM COMPLEXING AGENTS IN THE FORM OF VANADATES (TB4O7 AND IN2O3)

Vanadium tends to form thermally stable orthovanadates with different cations, which include Tb and In. With a view to establishing the effect of the presence of these modifier agents on the system $V_2O_5.ZrO_2$ compositions $0.2V_2O_5.0.1M_2O_3.ZrO_2$ (M=Tb,In) were prepared. The precursory oxides Tb_4O_7 or In_2O_3 were mixed with NH_4VO_3 and zirconia in a ball mill with acetone as a dispersing agent. The dry powder was calcined at 1100°C/1h and 1200°C/2h.

Table IV details the diffraction and colorimetry results. The data indicate crystallisation of $TbVO_4$ at the two temperatures and production of the yellow-orange colour on calcining at 1200°C. With indium the results indicate serious difficulties in obtaining the colour; it acted as a process inhibitor in the different repetitions performed. Indium vanadate was only detected in the samples calcined at 1200°C.

Sample	M Precursor	1100°C/2h	1200°C/2h
M1	Tb_3O_7	Powder colour: light brown L*a*b*=87/1/27 XRD:M(m)$TbVO_4$(d)	Powder colour: yellow-orange L*a*b*=81/9/40 XRD:M(m)$TbVO_4$(d)
M2	In_2O_3	Powder colour: brown L*a*b*=97/2/12 XRD:M(m)	Powder colour: yellow L*a*b*=86/4/35 XRD:M(m)$InVO_4$(d)

Table IV. Results found with samples $0.2V_2O_5.0.1M_2O_3.ZrO_2$. Peak intensity and crystalline phases detected: md(very weak), d(weak), m(medium), f(strong), mf(very strong), M(monoclinic zirconia).

4.4. MICROSTRUCTURAL STUDY AND MAGNETIC CHARACTERISATION

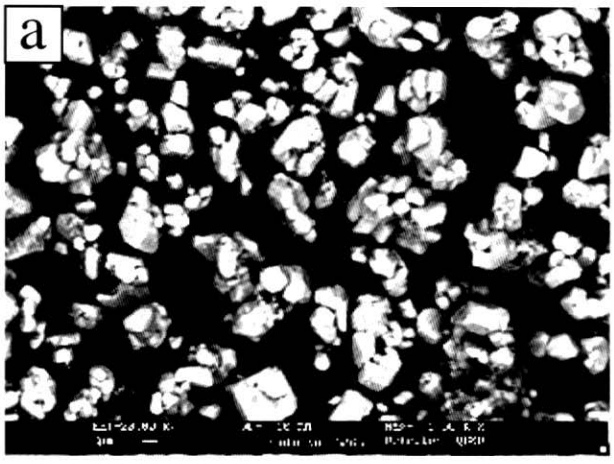
The foregoing studies indicate the existence of three types of coloration in the studied system V_2O_5-ZrO_2.

(I) greenish yellow coloration with zirconia diffraction peaks of relatively low intensity, with CIEL*a*b* values around 90/1/25 in the pieces glazed at 5% in monoporosa. They are the samples calcined at low temperature.

(II) lemon yellow coloration with development of peaks of variable zirconia, with CIEL*a*b* values around 95/0/30 in the pieces glazed at 5% in monoporosa. These are samples calcined at 1100°C with not completely transformed zirconia but it also appears with samples calcined at 1200°C.

(III) yellow-orange coloration in which the zirconia phase presents more intense peaks than in the previous colorations, with CIEL*a*b* values around 80/9/40 in monoporosa. This represents the coloration of interest as a ceramic pigment. The calcination at temperatures that guarantee the transformation of the zirconia is not a sufficient condition, albeit a necessary one, to obtain these colorations.

The SEM-EDX studies carried out with the different samples indicate a clear microstructural differentiation between the three colours, as Figure 4 shows. In the sample of scarce colouring interest, the greenish yellow one, micrograph 4.a exhibits relatively small particles, of about 2-4 μm, rounded and monolithic. The lemon yellow sample shows, together with a fraction of the order of 30% of these small particles, the presence of crystalline aggregates of monoclinic prisms, which also tend to adopt a prism-shape form, with average heights of 8 μm and 5 μm widths (Fig. 4.b). Finally, sample II yellow orange exhibits a particulate in which prism-shaped crystals are aggregated with sizes around 10 μm (Fig. 4.c). Reiterated analysis of the samples in different vanadium fields by means of Energy-Dispersive X-Ray Analysis (EDX) indicates the presence of a similar quantity of surface vanadium in all the samples (around 1.5%), although in the samples in which vanadium was retained, complexing it as terbium or indium vanadates, proportions of 8 % were reached, given the presence of particles of these vanadates.



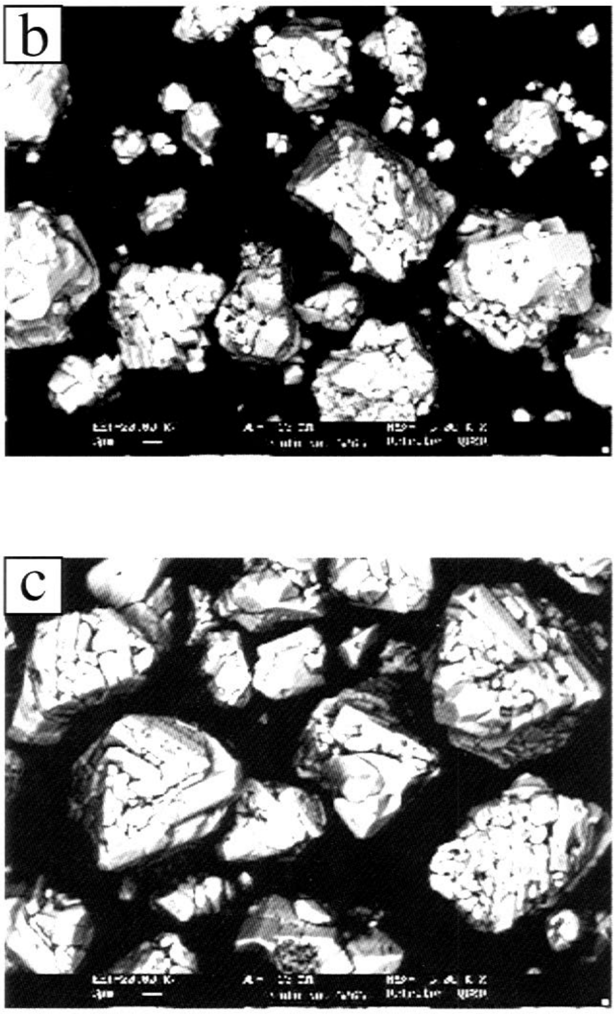


Figure 4. Electron micrographs of the washed samples: (a) low intensity greenish yellow; VO at 1100°C/2h, (b) lemon-yellow; SO at 1200°C/2h, (c) yellow orange; MO at 1200°C/2h.

Finally, Table V sets out the lattice measurements of the monoclinic zirconia unit cell in three representative samples of the three identified types of coloration. It is observed that although in all the cases shrinkage of the crystalline network of zirconia monoclinic can be detected, which can be interpreted by entrance in solid solution of a certain vanadium proportion (IV) in the network[4,5]. The fact of always taking place, independently of the developing colour excludes this vanadium in solid solution as being responsible for the coloration. The magnetic characterisation of the samples carried out in an AGFM magneto-susceptometer of variable field gradient and 10 μemu sensitivity, indicates that diamagnetic substances are involved (magnetic mass susceptibility –0.45 μemu/g) except in the modified samples of vanadates where the presence of the terbium vanadates makes the samples paramagnetic (magnetic mass susceptibility –0.45 μemu/g) by the presence of the paramagnetic ion Tb^{3+}([Xe]$4f^8$). The diamagnetic character of the samples would eliminate V4+ in solid solution as a significant agent in the generation of the observed coloration. Now in accordance with the previous microstructural results, colour is manifested in association with a "capturing" or encapsulating mechanism of the liquid, rich in V_2O_5, in equilibrium with the tetragonal zirconia crystals at high temperatures by these same crystals, in accordance with the stages indicated in Figure 5:

	ZrO_2	Yellow-Orange (MO 1200ºC)	Lemon-yellow (M1 1100ºC)	Greenish yellow (V0 1100ºC)
a(Å)	5.314	5.314(4)	5.313(3)	5.311(2)
b(Å)	5.213	5.208(4)	5.205(3)	5.209(1)
c(Å)	5.147	5.146(3)	5.147(2)	5.144(1)
β	99.22	99.22	99.22	99.22
V(Å^3)	140.70	140.6	140.5	140.5

Table V. Lattice parameters of different samples $0.4V_2O_3ZrO_2$.

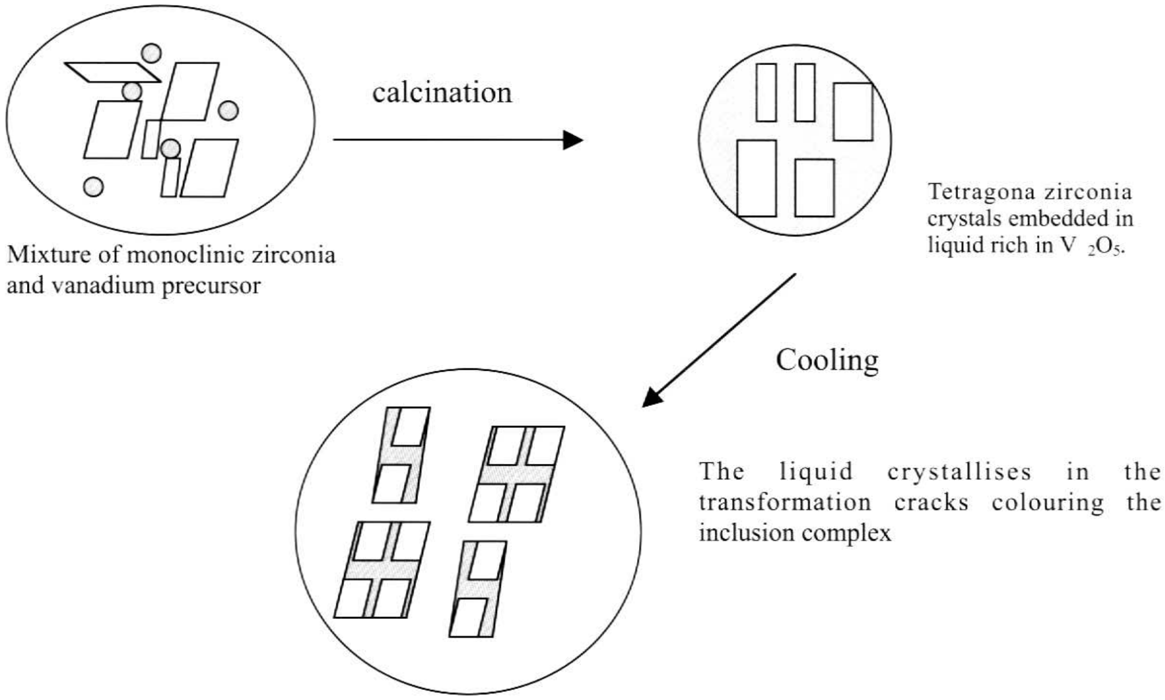


Figure 5. Model of yellow zirconia-vanadium pigment formation.

(a) Formation of tetragonal zirconia.

Once the zirconium pyrovanadate has decomposed, on increasing the temperature, the monoclinic zirconia becomes tetragonal, which remains in equilibrium with a liquid rich in V_2O_5.

(b) Tetragonal-monoclinic transformation and liquid inclusion by capillarity.

On cooling the tetragonal crystals become monoclinic, cracking as a result of the stresses produced by shrinkage. The liquid is absorbed by capillarity inside the particulate.

(c) Crystallisation of the occluded phases and formation of inclusion complexes.

The phases crystallise inside the particles generating additional stresses that can break up the particulate and set the vanadium pentoxide free; it is also possible for ZrV_2O_7

to recrystallise and for the eutectic reaction to occur at 690ºC. Depending on the conditions, the occluded colouring phases can stay in encapsulating particulates, true V_2O_5 inclusion complexes in zirconia as in Fig. 4.c (yellow-orange coloration), or they can be de-encapsulated when the inclusion complexes disintegrate, as shown in Fig. 4.a (colour loss), or so partially (yellow colourings of Fig. 4.b).

5. CONCLUSIONS

In the case of the encapsulated or heteromorphic pigments, intensely coloured powders cannot ensure colour generation in the glazes. In the heteromorphic pigments based on a synchronism mechanism in the crystallisation and/or sintering of the phases involved, complexing and precursor design are techniques that can improve encapsulating efficiency when this takes place in the heating phase. In contrast, if the encapsulation develops by a phase transition mechanism, the chemical precursor design is not relevant, since the pigment is structured in the cooling of the system.

ACKNOWLEDGEMENTS

the authors thank the CICYT for the funding received for the work (project MAT98-0392).

REFERENCES

[[1] V. LAMBIES, J.MA. RINCÓN, Study of the Mechanism of Formation of a Zircon-Cadmium Sulphoselenide Pigment, Trans. J. Br. Ceram. Soc., 80, 105-108,1981.

[2] G.MONRÓS, J.CARDA, M. A.TENA, P.ESCRIBANO, J.ALARCÓN., "Effects of ZrO_2 precursors on the synthesis of V-$ZrSiO_4$ solid solutions by the sol- gel method ".Journal of Mater. Sci. 27(1992)351-357.

[3] M. LLUSAR, J. CALBO, J.A. BADENES, M.A. TENA, G. MONRÓS, "Synthesis of iron zircon coral by coprecipitation routes", J. of Mater. Sci., 35(2000)1-11.

[4] P. TARTAJ, J. SERNA, J. SORIA, M. OCAÑA, J. MATER. Res. 13(1998)413.

[5] J. ALARCÓN, Synthesis and Characterisation of vanadium-containing ZrO_2 solid solutions pigmenting system from gels, J. of Mat. Sci. 36(2001)1-7.

[6] B.S. CHEREPANOV, Steklo i Keramika 2281965)8-12.

[7] G. Monrós, J.Carda, M.A. Tena, P. Escribano, J. Alarcón, Synthesis of ZrO_2-V_2O_5 Pigments by Sol-Gel Methods, Br. Ceram. Trans. J., 90(1991)157-160.

[8] G. MONRÓS, M. C. MARTÍ, J. CARDA, M.A. TENA, P. ESCRIBANO, M. ANGLADA, "Effect of hydrolysis time and type of catalyst on the stability of tetragonal zirconia-silica composites synthesized from alkoxides", J. Mater. Sc., 28(1993)5852-62.

[9] J. BADENES, E. CORDONCILLO, M. A. TENA, P. ESCRIBANO, J. CARDA, G. MONRÓS, "Análisis de las variables de síntesis del pigmento yellow de praseodimio en circón", Bol. Soc. Esp. Ceram. Vidr, 34 (3)(1995)147-152.