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Preparation of YVO_4 powder from the $Y_2O_3 + V_2O_5 + H_2O$ system by a hydrolysed colloid reaction (HCR) technique

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Prior to the formation of YVO_4 in the $Y_2O_3+V_2O_5+H_2O$ system, two intermediate, partially hydrophobic, complex colloidal mixtures with metastable characteristics can be produced at room temperature and atmospheric pressure. The ball-milled system, having both hydrophobic and hydrophilic species, transforms into the stable yttrium orthovanadate phase due to intensive hydrolysis. At room temperature an orange mixture (possessing dispersed Y_2O_3 and $4Y_2O_{3-p}(OH)_p^{p+} \cdot 2VO_3^-$, $Y_2O_{3-p}(OH)_p^{p+} \cdot 6VO_3^- \cdot xH_2O$-like heteroaggregations) formed by 20 h mixing at pH ca. 4.0 transforms slowly, another red–brown heavily flocculated colloidal mixture (with dispersed Y_2O_3 and $Y_2O_{3-p}(OH)_p^{p+} \cdot V_{10}O_{28}^{6-} \cdot yH_2O$-like aggregation) formed by 70 h mixing at pH ca. 4.5 transforms rapidly into YVO_4 in water. During additional mixing of highly diluted red–brown mixtures this transformation can be completed at room temperature. At elevated temperatures (50–95 °C) the orange mixture precipitates into a red–brown decavanadate-type precipitatium which subsequently can also rapidly hydrolyse into an orthovanadate phase in the diluted aqueous systems. Both vanadium excess meta- and decavanadate-type aggregations exhibit amorphous character by X-ray diffraction.

The semi-hydrophobic colloidal structure can modify the dissociation mechanism, which prevents the system from returning to the starting oxides, and gives a new HCR technique for YVO_4 preparation with a simple hydrolysis process at low temperatures and atmospheric pressure.

1. Background

Yttrium orthovanadate (YVO_4), in powder form, is a very attractive material for use as a red phosphor with trivalent Eu^{3+} dopant [1, 2] in colour television and cathode ray tube (CRT) applications, and is an excellent polarizer [3, 4] and laser host material [5, 6] in single crystal form. For these applications, however, homogeneous, high quality, oxygen deficiency-free YVO_4 is required. It is a well known fact that vanadium pentoxide (V_2O_5) vaporizes readily above its melting point (690 °C), causing incongruent changes in both the vanadium and oxygen stoichiometries [7–9]. In several cases, the oxygen deficiency caused by a high temperature process can cause problems in the optical application of YVO_4 [9].

Three different methods can be used to produce oxygen deficiency-free YVO_4: (1) the special flux technique [10]; (2) the hydrothermal reaction technique [2]; and (3) the low temperature ($T < 100\,°C$) aqueous solution technique. The wet techniques are strongly recommended for improvement of phosphors in high-resolution displays and miniature CRTs [11], since the higher temperature solid-state reaction techniques produce relatively large grain size materials in addition to oxygen defect colour centres. The reduction of particle size by mechanical grinding results in crystal particle damage and lower luminescent efficiency.

In 1965 Arbit and Serebrennikov [12] first produced YVO_4 in aqueous solution by reacting yttrium nitrate and ammonium metavanadate according to Equation 1:

$$Y(NO_3)_3 + NH_4VO_3 + H_2O \rightarrow YVO_4 + NH_4NO_3 + 2\ HNO_3 \qquad (1)$$

Using this approach, in 1972 Krylov *et al.* [13] patented a technique for industrial applications. In 1969 Popov *et al.* [14] produced YVO_4 from an aqueous solution of yttrium nitrate and potassium orthovanadate by Equation 2:

$$K_3VO_4 + Y(NO_3)_3 \rightarrow YVO_4 + 3KNO_3 \qquad (2)$$

In 1971 Ropp and Oakley [15] patented a wet preparation technique in which the V_2O_5 and Y_2O_3 oxides were dissolved in diluted HCl, and the YVO_4 was precipitated in solution with $NaOH + NaBIO_3$. In 1971 Ropp [16] patented another method, where V_2O_5 and Y_2O_3, dissolved in dilute HCl, precipitated in solution with $H_2O_2 + NH_4OH$. With this technique the precipitation contained the formed NH_4Cl. In 1972, another aqueous solution technique for

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orthovanadate formation (MVO_4) was realized by Ivakin, Fotiev and co-workers in strong basic solution (pH = 14) [2, 17]. In 1977 the chemistry of vanadium in aqueous solution was investigated by Ropp and Carroll [18], over the entire pH range for rare earth precipitates. In their work the investigations and the production of different yttrium–vanadium precipitates (including YVO_4) were performed by titration of VO^{2+} plus rare earth ions in strong HCl acid solution with NaOH (or NaOH plus H_2O_2). Subsequently (1982–1987) Zaslavskaya and Nakhodnova investigated the aqueous Y–V–O system [19–22], paying special attention to the formation of ortho-, meta- and decavanadates. Later (1988) Yamaguchi *et al.* [23] prepared YVO_4 powder by an alkoxy method and found that YVO_4 can be prepared by simultaneous hydrolysis of yttrium and vanadyl alkoxides, followed by washing and drying.

This brief survey of previous works shows that hydrolysed colloidal-type mixtures of the aqueous $V_2O_5 + Y_2O_3 + H_2O$ system have not been investigated for the production of YVO_4. By utilizing the readily hydrolysable characteristics of the metastable complexes in this system, a very simple and promising technique for the preparation of small particle size YVO_4 powder, was obtained at low temperature and atmospheric pressure.

2. Experimental procedure

To produce the stoichiometric YVO_4 compositions, 1/30 mol V_2O_5 (99.9%) and 1/30 mol Y_2O_3 (99.99%) (Johnson Matthey Chemical) were weighed with various quantities (30, 60 or 90 ml) of deionized water. These mixtures, with alumina grinding media (40 pieces of $D = 5 \times 5$ mm balls), were placed in polyethylene bottles (125 ml with high density walls) for ball milling. For production of the colloidal mixture, the mixing–milling (hereafter referred to as mixing) was carried out by a ball-mill technique typically used in ceramic preparation processes (Fig. 1). The mixing was conducted at 120 r.p.m. for various times (4, 20 or 70 h). All experiments were carried out in air at atmospheric pressure.

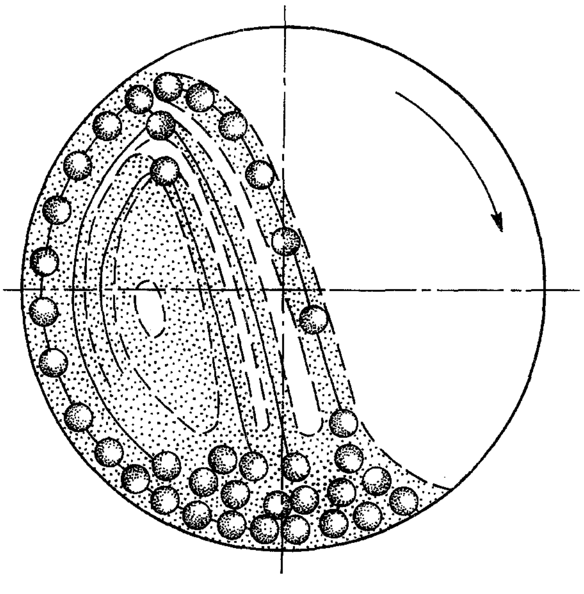

Figure 1 Scheme of ball mill for production of colloidal mixtures.

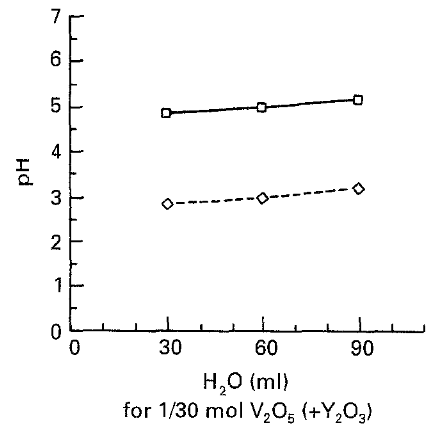

Figure 2 pH values in $V_2O_5 + Y_2O_3 + H_2O$ (□) and $V_2O_5 + H_2O$ (◇) system with different dilutions; after 1 h soaking without mixing.

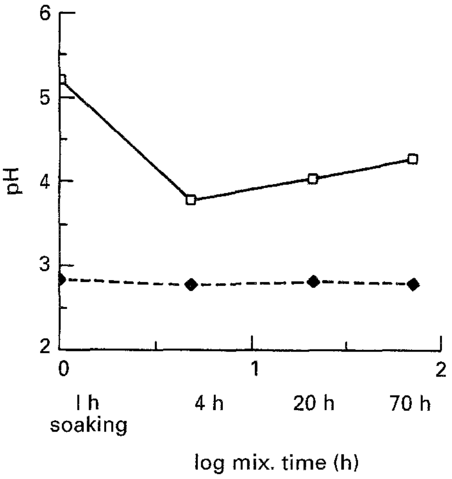

Figure 3 pH values in $V_2O_5 + Y_2O_3 + H_2O$ (□) and $V_2O_5 + H_2O$ (◆) aqueous mixtures after different mixing times; specimens prepared from 1/30 mol V_2O_5 (+ Y_2O_3) + 90 ml H_2O.

Since acidification of the $V_2O_5 + Y_2O_3 + H_2O$ aqueous system plays an important role in the formation of complex colloids, the pH behaviour of these mixtures was investigated first. In addition, the formation of colloidal-type mixtures and precipitates, and their hydrolysis process, were correlated with mixing time, solution temperature and concentration.

Prior to mixing, the first measurements were taken 1 h after weighing the components with different dilutions at 25 °C (Fig. 2). During the mixing process the temperature was stabilized at 38 °C, so subsequent measurements were conducted at 38 °C. After 20 h of mixing the specimen, diluted in 30 ml water, was too viscous for exact pH measurements. After 70 h of mixing the specimen, diluted with 60 ml water, was also too concentrated for pH measurements and the colour changed from orange to red–brown. Thus, influence of 70 h mixing on the pH value could be measured only in the specimen diluted with 90 ml water (Fig. 3).

The temperature dependence of pH in the colloidal-type orange mixture, formed in 90 ml water after 20 h mixing, was investigated between 35 and 90 °C (Fig. 4). Measurements were made in 5 °C increments with continuous heating (2 °C min^{-1}) and stirring.

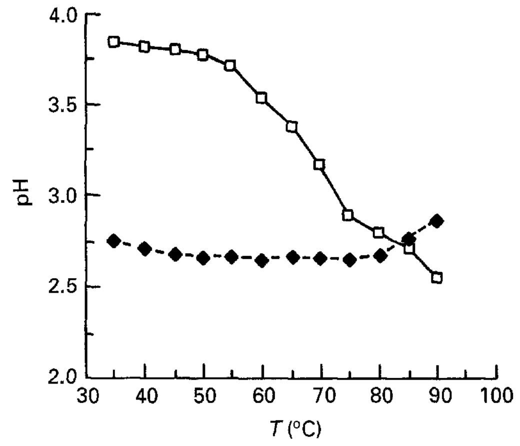

Figure 4 Temperature dependence of pH values in V_2O_5 + Y_2O_3 + H_2O (□) colloid and V_2O_5 + H_2O (◆) suspension systems premixed for 20 h; specimens prepared from 1/30 mol V_2O_5 (+ Y_2O_3) and 90 ml H_2O.

The previously mentioned pH measurements were also repeated in a pure V_2O_5 aqueous system – experimental conditions were identical for each specimen (Figs 2–4). Both types of diluted wet mixtures (orange and red–brown) were metastable and transformed to YVO_4 during the drying process. The time of formation to YVO_4 from the orange mixture was investigated at 90, 70, 45 and 25 °C with different dilutions. In each case the reactions were conducted without stirring in uncovered beakers (250 or 80 ml Pyrex), facilitating faster drying. After complete hydrolysis, and drying at the above mentioned temperatures, the reaction was complete, and some samples of obtained white YVO_4 powder were calcined at 800 °C for 2 h to increase the average particle size.

The impact of the further mixing of the red–brown mixture (subsequently diluted by 10 times) was also investigated. Similarly, to achieve an accelerated reaction at room temperature, a highly diluted sample was prepared from 1/150 mol V_2O_5 and 1/150 mol Y_2O_3 in 180 ml H_2O. This mixture, with larger size alumina grinding media (40 pieces of $D = 10 \times 10$ mm balls), in a polyethylene bottle (250 ml) was milled at 160 r.p.m. for 120 h.

For characterization of above mentioned aqueous mixtures a Fisher Scientific Accumet 910 pH meter was used to determine the pH values. For investigation of orange and red–brown colloid-like mixtures, 0.5 ml specimens were filtered and dried in air without hydrolysing at room temperature. The non-hydrolysed orange and red–brown powders, as well as reacted white YVO_4 and calcined YVO_4 powders, were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The XRD data was produced by Scintag Pad-V/VAX 3100 computerized diffractometer with CuK_α radiation ($\lambda = 0.154059$ nm). Energy dispersive spectroscopy (EDS), KEVEX 8000 Microanalyser with an ISI DS 130 scanning electron microscope, was utilized to identify the different phases and to investigate the microstructure in the above mentioned powder samples. Since these powders are good insulators, the SEM samples were coated with gold to obtain acceptable SEM pictures and analysis.

3. Results and discussion

3.1. Colloidal mixtures and their transformations into YVO_4

Non-ideal, complex colloidal mixtures were prepared from the $Y_2O_3 + V_2O_5 + H_2O$ system by the ball-milling technique. The mixtures in the present study did not form ideal colloids since, on the one hand, they consisted of hydrophobic and hydrophilic colloid species and, on the other, their average particle size was in the range of 0.1–2 µm between colloids and suspensions. The hydrophilic vanadyl ions markedly determine both the formation of hydrophobic flocculation and the hydrolysis process.

Investigation of the acidifications in both $Y_2O_3 + V_2O_5 + H_2O$ and $V_2O_5 + H_2O$ aqueous mixtures showed significant differences. The oxide particles in water without mixing or short-term mixing did not form a colloidal mixture because of their large average particle sizes ($\gg 0.1$ µm). The presence of Y_2O_3 caused a strong change in pH value; shifting the acidity from pH 3 to 5, as seen in Fig. 2. The pH of $V_2O_5 + Y_2O_3$ aqueous mixtures can be also changed, by long-term intensive mixing and temperature variation, from an initial pH of 5 to 2.5 (Figs 3 and 4). No significant pH change was observed after different mixing times in the simple V_2O_5 aqueous mixtures (Fig. 3). A similar effect was also obtained for temperature dependence of pH (Fig. 4). In contrast, the pH of the Y_2O_3 + V_2O_5 orange colloidal system, mixed for 20 h, showed a substantial pH decrease with increasing temperature (Fig. 4), while the mixture precipitated and changed its colour to red-brown. This precipitate was rapidly formed between 85 and 90 °C, where the pH value was 2.55. After the completion of the precipitation at 90 °C the pH increased to 3.5 and displayed no further significant temperature dependence. The red–brown precipitate, upon the addition of enough water, transformed into white YVO_4 at 90 °C, and upon completion of YVO_4 formation, the pH increased and stabilized at 5.6. Without enough hydrolysing media the reaction could not be completed, and the mixture dried to red–brown powder.

During the mixing procedure the colloidal mixtures absorbed water and the less diluted specimens became too viscous. Two types of water absorption were observed: firstly, at the formation of the orange colloidal dispersion (after 20 h mixing); and secondly, at the formation of the red-brown colloidal mixture (after 70 h mixing). The specimen diluted in 30 ml water after 20 h became a very viscous hydrophobic mixture with an orange colour, in contrast with ideal hydrophobic colloids [26, 43]; the specimen diluted in originally 60 ml water after 70 h mixing became a viscous red–brown colloid.

These observations agree with the results of Ropp and Carroll [18], as well as Zaslavskaya and Nakhodnova [22]. Ropp and Carroll reported the formation of orange–yellow yttrium trimetavanadate ($YV_3O_9 \cdot xH_2O$) with less crystal water in pH 3.5–5.5 solutions and a red–brown yttrium decavanadate intermediate phase ($Y_2V_{10}O_{28} \cdot 25H_2O$) with more water in pH 1.5–3.0 solutions. Zaslavskaya and Nakhodnova obtained a $YV_3O_9 \cdot (4\text{–}6)H_2O$ chemical formula for their trimetavanadate species. It is obvious from these data that the hydrous decavanadates possess about five times more water than the hydrous metavanadates. Present observations, on both colours (orange or red–brown) and water absorptions, are in agreement with the literature data [18, 20, 22], which indicates that the orange colloidal mixture with trimetavanadate-type complex dominance, and the red-brown colloidal dispersion having decavanadate-type complex dominance, are highly probable. However, the literature is not consistent in the structures of these vanadates. Ropp and Carroll [18] reported amorphous structures for both meta- and deca-type vanadates, while Zaslavskaya and Nakhodnova [22] and Rigotti *et al.* [24] obtained crystalline structures.

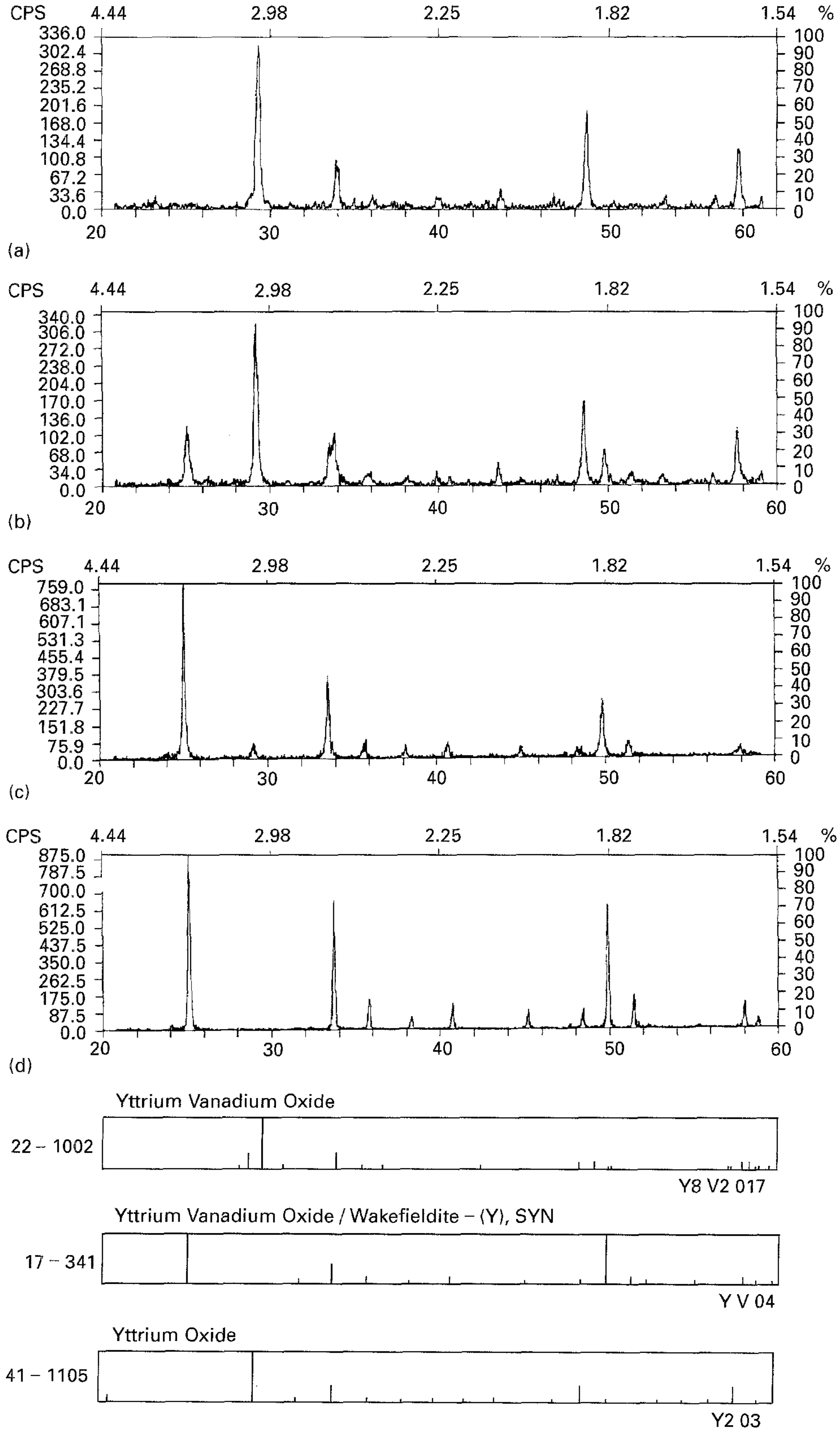

Figure 5 Powder X-ray diffraction patterns of orange (a) and red–brown (b) dried colloidal mixtures, reacted white YVO_4 powder after hydrolysis (c) and calcined white YVO_4 powders (d). The 22–1002, 17–341 and 41–1105 JCPDS files [25] also can be seen to identify the obtained crystalline phases.

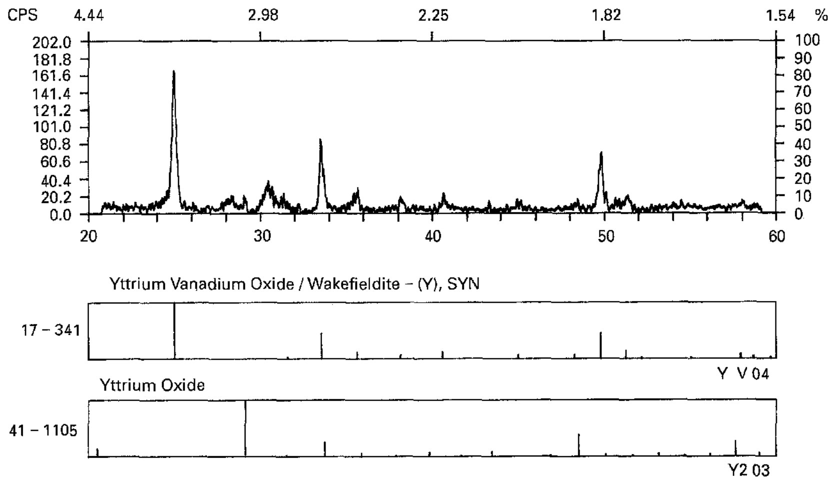

Figure 6 Powder X-ray diffraction pattern of YVO_4 formed at room temperature by intensive mixing and hydrolysis of diluted red–brown colloidal mixture.

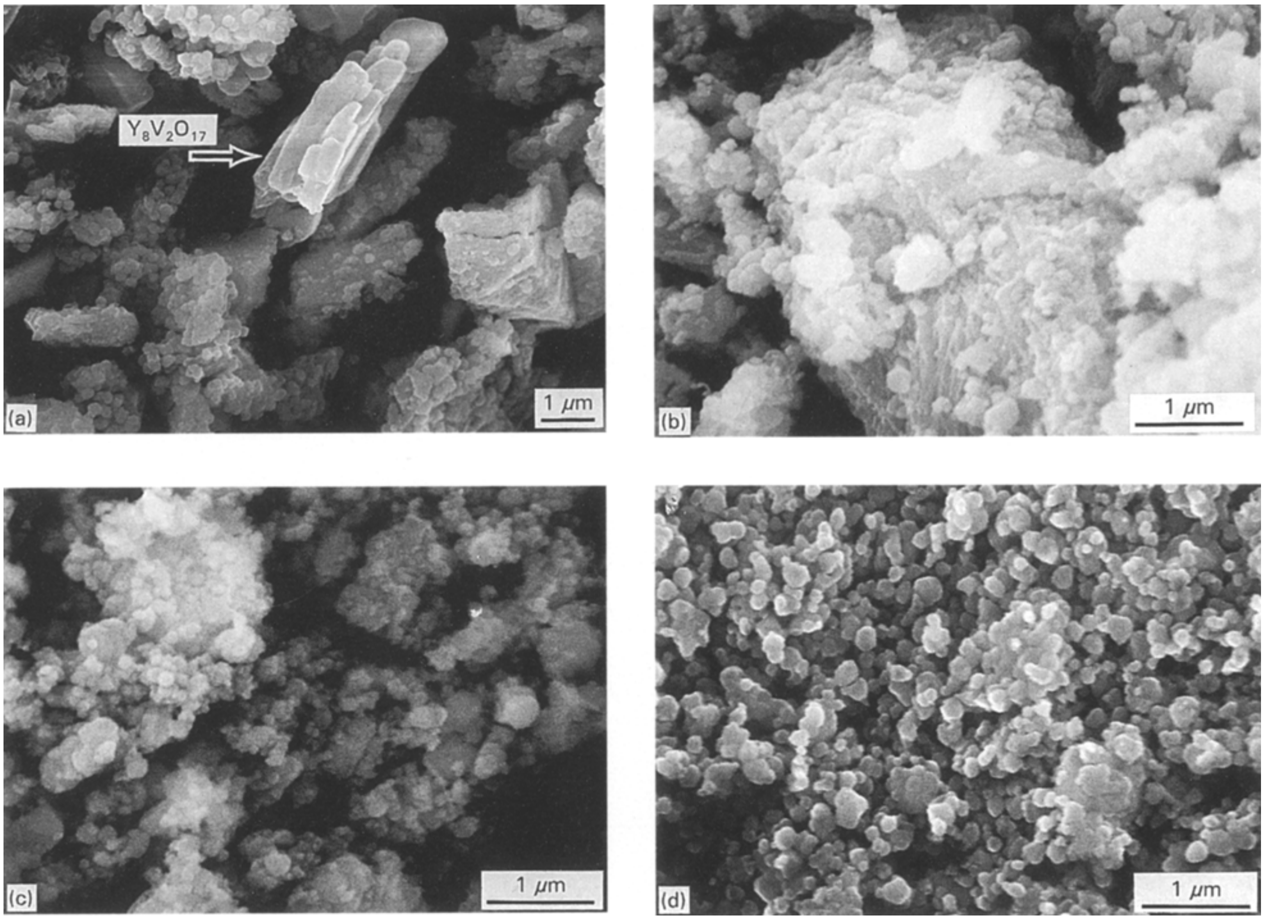

Figure 7 SEM micrographs of dried orange colloidal mixture (a) dried red–brown precipitation (b), white YVO_4 powder after hydrolysis (c) and calcined YVO_4 powder (d).

In the present work no crystalline structure for these intermediate vanadates was observed by XRD patterns, Fig. 5. The orange specimen exhibited only Y_2O_3 and $Y_8V_2O_{17}$ crystalline phases (Fig. 5a), in contrast with the precipitated red-brown sample which already indicated a little YVO_4 crystalline phase over Y_2O_3 and $Y_8V_2O_{17}$ phases (Fig. 5b). Y_2O_3 and $Y_8V_2O_{17}$ phases, in small concentrations, were not distinguishable by XRD, since they have lines close to each other [25], (Figs 5 and 6). EDS measurement could identify the presence of both crystalline $Y_8V_2O_{17}$ phase particles (Fig. 7a) and Y_2O_3, but trimetavanadate–decavanadate phases were still indistinguishable. The SEM micrograph in Fig. 7a shows one $Y_8V_2O_{17}$ crystal piece in the dried nonhydrolysed orange powder. The obtained EDS data for this crystal piece was Y : V = 3.5 : 1 atomic ratio in contrast with surrounding particles, where Y : V ca. 1 : 2.5 ratio

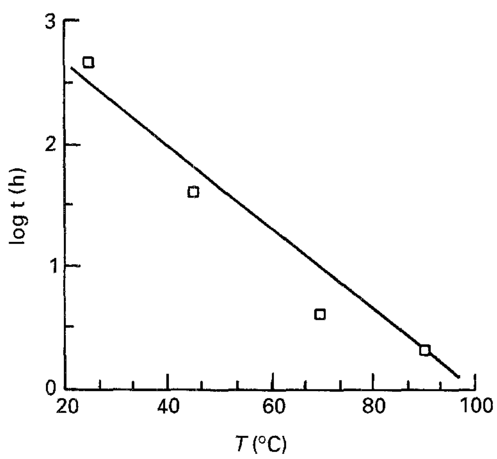

Figure 8 Dependence of YVO_4 formation time on the preparation temperature in the originally orange colloidal mixture.

were measured. In very limited areas Y_2O_3 was also indentified. The YVO_4 particles were already observed in the red–brown non-hydrolysed specimen (Fig. 7b). Fig. 7b exhibits the formation of small pigment-type YVO_4 particles on the surface of large size Y–V–O complex flocculation (probably decavanadate type). Since YVO_4 formation starts on the surface region of the aggregations due to the gradual hydrolysis process, the EDS measurement could not to distinguish the Y : V = 1 : 3 ratio (yttrium metavanadate-type aggregation) of Y : V = 1 : 4 ratio (yttrium decavanadate-type aggregation). Due to hydrolysis of the orange colloidal dispersion at 90 °C, white YVO_4 powder with 0.1 µm average particle size was obtained (Fig. 7c). Subsequently, the high temperature (800 °C for 2 h) calcining procedure increased the average particle size up to 0.2–0.3 µm (Fig. 7d).

XRD spectra of YVO_4 (after hydrolysis), Fig. 5c, indicates that the reaction was complete. Very small Y_2O_3 and/or $Y_8V_2O_{17}$ XRD lines indicate that small amounts of these phases remained, which were totally eliminated by the calcining process (Fig. 5d).

The hydrolysis procedure and its completion depend on the (drying) temperature. The orange colloidal-type mixtures at different temperatures require different hydrolysis processing times, Fig. 8. Although the complex orange mixture can transform into YVO_4 at room temperature, the whole process requires a long time (five weeks) for completion and the reaction can be difficult to control. During transformation, at higher temperatures (45, 75 or 90 °C) the trimetavanadate-type orange mixture precipitates to the decavanadate-type red–brown precipitatum which hydrolyses more rapidly in YVO_4. The pure single crystalline YVO_4 phase (without small quantities of Y_2O_3 and/or $Y_8V_2O_{17}$) was achieved at room temperature by additional mixing of the subsequently diluted red–brown mixture (Fig. 6). In contrast with this observation, long-term mixing (120 h) of the highly diluted $Y_2O_3 + V_2O_5 + H_2O$ starting system did not give a similarly good quality of single-phase YVO_4.

It was established that both colloidal (orange and red-brown) mixtures exhibit "one way" metastable behaviour toward YVO_4, since returning to starting Y_2O_3 and V_2O_5 oxides was not observed.

3.2. YVO_4 reaction by the hydrolysed colloid reaction (*HCR*) technique and its possible interpretation

The interpretation of the above observed processes is quite difficult due to the complexity of hydrophobe flocculation and hydrophil isopolivanadate anions which play a dominant role in the $Y_2O_3 + V_2O_5 + H_2O$ colloidal mixture. However, the experimental observations and the relevant literature data of vanadate anions, with reasonable speculative considerations, can produce an acceptable interpretation for this new YVO_4 reaction technique.

The simplified scheme of the hydrolysed colloid reaction (HCR) technique applied to YVO_4 can be seen in Table I. A,B substances (i.e. Y_2O_3, V_2O_5) in water are partially ionized by the hydrolysis I process and form A'^+ and B'^+ species. However, this process is still a reversible transformation. Subsequently, the ball-milling procedure forms both hydrophobic and hydrophilic type colloids in the $Y_2O_3 + V_2O_5 + H_2O$ aqueous system. A small amount of V_2O_5 can only form hydrophilic (vanadyl ion) species, because the major part of vanadium oxide and yttrium oxide particles are insoluble in water and participate in the formation of a hydrophobic colloid. The intensive collisions between these particles create a polymeric flocculant by complex bonds of different surface adsorption effects. The forces can be considered as electrostatic (coulombic), dipole attraction, London–Van der Waals, hydrophobic association, and chemical, coordination and hydrogen bondings [26, 43]. Although the exact bonding mechanism is not known, it is probable, in this case, that it is determined by the features of surrounding vanadyl anions. However, it is evident that this colloid formation is an irreversible process. Subsequently, metastable-type colloidal heteroaggregations ($A'^+.B'^+$) are formed in the mixture,

TABLE I. Scheme of hydrolysed colloid reaction (HCR) technique.

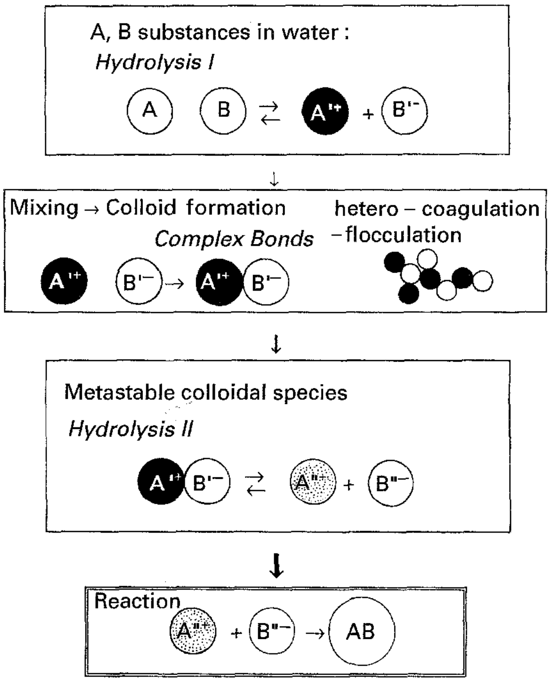

TABLE II Typical reactions in aqueous vanadium (V) system

No.	Reaction	Vanadium concentrations (g atom l^{-1})	Ref.
1	$V_2O_5 + 2H^+ \leftrightarrows 2VO_2^+ + H_2O$		[31]
2	$VO_2^+ + H_2O \leftrightarrows HVO_3 + H^+$	6×10^{-4}–1×10^{-7}	[32–34]
3	$HVO_3 \leftrightarrows VO_3^- + H^+$	6×10^{-4}–1×10^{-7}	[32, 33]
4	$3VO_3^- \leftrightarrows V_3O_9^{3-}$	3.6×10^{-2}–2.8×10^{-4}	[35]
5	$V_3O_9^{3-} + H_2O \leftrightarrows 3HVO_4^{2-} + 3H^+$	8×10^{-2}–6.25×10^{-4}	[17]
6	$HVO_4^{2-} + H^+ \leftrightarrows H_2VO_4^-$	1×10^{-2}–1×10^{-4}	[36]
7	$H_2VO_4^- + H^+ \leftrightarrows H_3VO_4$	1×10^{-2}–1×10^{-4}	[36]
8	$10VO_2^+ + 8H_2O \leftrightarrows H_2V_{10}O_{28}^{4-} + 14H^+$	1×10^{-2}–1×10^{-4}	[37–39]
9	$H_2V_{10}O_{28}^{4-} \leftrightarrows HV_{10}O_{28}^{5-} + H^+$	1×10^{-1}–2×10^{-3}	[37–39]
10	$HV_{10}O_{28}^{5-} \leftrightarrows V_{10}O_{28}^{6-} + H^+$	1×10^{-1}–2.5×10^{-3}	[29]
11	$3HV_{10}O_{28}^{5-} + 6H_2O \leftrightarrows 10V_3O_9^{3-} + 15H^+$	1×10^{-2}–5×10^{-3}	[36]

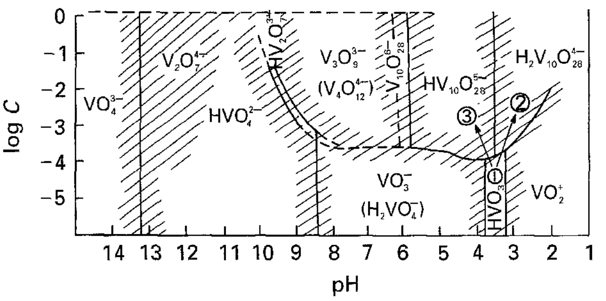

Figure 9 Concentration and pH ranges of stability of isopolyvanadate anions (after [17, 42]). with ①–② and ①–③ transformations.

which hydrolyse further by hydrolysis II. The obtained A''^+ and B''^- species react to form AB (i.e. YVO_4), with irreversible characters. It should be emphasized that hydrolysis I is a very important prerequisite for metastable-type colloid formation, in contrast with the YVO_4 reaction, where hydrolysis II becomes the dominant process.

Vanadium pentoxide in water produces an acidic solution by formation of VO_2^+ species (see reaction 1 in Table II). (The most important reactions of vanadyl anions are collected in Table II with many references.) Many reports have mentioned that different vanadate ion species in aqueous solution are dependent on pH. Britton [27] and Britton and Welford [28] observed three typical inflexion points on the titration curve of alkali metavanadate ($NaVO_3$), and interpreted them as different ionization states of vanadic acid (H_3VO_4).

Other works (see Table II, Fig. 9 [40, 41]) have mentioned VO_2^+, VO_3^- (or $H_2VO_4^-$), HVO_4^{2-}, $V_3O_9^{3-}$, $V_{10}O_{28}^{6-}$, $H_2V_{10}O_{28}^{5-}$, $H_2V_{10}O_{28}^{4-}$, $V_4O_{12}^{4-}$, $HV_2O_7^{3-}$, $V_2O_7^{4-}$ ions, in addition to VO_4^{3-} and HVO_3 vanadate species, at various pH values.

After formation of VO_2^+ ions, the VO_2^+ species produce HVO_3 vanadic acid molecules in the aqueous solution by reaction 2 (in Table II). During the addition of Y_2O_3 oxide to this vanadic acid solution, the acidity is significantly reduced; the pH value increased from 3 to 5 (Fig. 2) due to the reaction described by Equation 3:

$$Y_2O_3 + p(HVO_3) \leftrightarrows Y_2O_{3-p}(OH)_p^{p+} + pVO_3^-$$

$$0 \leq p \leq 3 \qquad (3)$$

Statistically, p molecules of HVO_3 can interact with one molecule of Y_2O_3 hydrophobic particle, which is protonized with different average ionization levels. During mixing, when the substances are comminuted by ball milling, the complex $Y_2O_3 + V_2O_5 + H_2O$ system exhibits further pH change (Fig. 3), as was previously mentioned. Although the $Y_2O_3 + V_2O_5 + H_2O$ system is more complex than the $V_2O_5 + H_2O$ system, it is obvious that the different types of vanadyl ions presented in Fig. 9 play dominant roles in the formation of different complex colloidal mixtures, depending on pH, in the complex $Y_2O_3 + V_2O_5 + H_2O$ system. Some hours of mixing in the ball mill forms metastable yttrium and vanadium excesses (see Equation 9), a hydrophobic (irreversible) colloidal mixture, and the nonaggregated, independent $Y_2O_{3-p}(OH)_p^{p+}$ species. The yttrium excess heteroaggregation can be described by Equation 4:

$$4Y_2O_{3-p}(OH)_p^{p+} + 2VO_3^- \rightarrow 4Y_2O_{3-p}(OH)_p^{p+} \cdot 2VO_3^- \qquad (4)$$

which can crystallize to $Y_8V_2O_{17}$ by Equation 5:

$$4Y_2O_{3-p}(OH)_p^{p+} \cdot 2VO_3^- \xrightarrow{\text{crystallization}} Y_8V_2O_{17} + k_1H^+ + l_1(OH)^- \qquad (5)$$

as observed in SEM examination of orange powder samples (Fig. 7a). Consequently, to avoid the yttrium excess phases (including Y_2O_3) in the final YVO_4 powder, additional mixing and hydrolysis are required. In these cases metastable $4Y_2O_{3-p}(OH)_p^{p+} \cdot 2VO_3^-$ aggregation and protonized species $Y_2O_{3-p}(OH)_p^{p+}$

further dissociate, as described for $p = 1$ average ionization states by Equations 6 and 7:

$$4Y_2O_2(OH)^+\cdot 2VO_3^- \leftrightarrows 4Y_2O_2^{2+} + 2VO_3^- + 4OH^- \qquad (6)$$

$$Y_2O_2(OH)^+ \leftrightarrows Y_2O_2^{2+} + OH^- \qquad (7)$$

giving suitable conditions for transformation into orthovanadate phases by reaction of Equation 8:

$$Y_2O_2^{2+} + 2VO_3^- \rightarrow 2YVO_4 \qquad (8)$$

These reactions are complete when the water dispersion medium has enough VO_3^- anion species due to hydrolysis.

The vanadium excess aggregations in the non-ideal orange colloid are amorphous, as seen from Fig. 5a. Their colour, acidity rate and EDS data indicate that this flocculation is a metavanadate-like substance, which can be originated by Equation 9:

$$Y_2O_{3-p}(OH)_p^{p+} + 6VO_3^- + xH_2O \rightarrow Y_2O_{3-p}(OH)_p^{p+}\cdot 6VO_3^-\cdot xH_2O \qquad (9)$$

The EDS data for the Y : V ratio in $Y_2O_{3-p}(OH)_p^{p+}\cdot 6VO_3^-\cdot xH_2O$ aggregations exhibited a similar value (Y : V = 1 : 2.5) to the crystalline $YV_3O_9\cdot xH_2O$ phase, which can resolve the contradiction of crystalline–amorphous characters described in the literature [18, 22, 24]. The obtained difference in Y : V ratios is in connection with the statistical feature of hydrolysation, protonization and aggregation processes.

It was observed that $Y_2O_{3-p}(OH)_p^{p+}\cdot 6VO_3^-\cdot xH_2O$ aggregations do not (or very slowly) transform into $2YV_3O_9\cdot xH_2O$ crystalline phase in contrast with $4Y_2O_{3-p}(OH)_p^{p+}\cdot 2VO_3^-$ aggregations, which could crystallize to $Y_8V_2O_{17}$ (Equation 5). The hydrolysation of metavanadate-like aggregation for the case in which $p = 1$ can be described by Equation 10:

$$Y_2O_2(OH)^+\cdot 6VO_3^-\cdot xH_2O \leftrightarrows Y_2O_2^{2+} + 6VO_3^- + xH_2O + OH^- \qquad (10)$$

in which the ionized $Y_2O_2^{2+}$ species give a prerequisite for transformation into YVO_4. However, the processes described by Equations 8–10 are very slow at room temperature, requiring about five weeks to react (see Fig. 8). At elevated temperatures, or longer mixing times, these characteristics are changed. As can be seen from Fig. 9, the HVO_3 acid occupies a limited region of the log C–pH anion stability diagram. Fig. 10a and b (after [17, 42]) show the distributions of the relative V concentration (α) versus pH value for HVO_3 and other vanadyl anions. It can be seen that the diluted solutions (10^{-5} mol [V] l^{-1}) (Fig. 10a) possess HVO_3 species around pH 3.5 [15], in contrast to the higher concentration solutions (10^{-2} mol [V] l^{-1}) (Fig. 10b) in which only two different types of decavanadyl acids ($HV_{10}O_{28}^{5-}$;$H_2V_{10}O_{28}^{4-}$) exist near pH 3 [29]. The orange colloidal mixtures precipitate between 45 and 90 °C and transform into red–brown $H_2V_{10}O_{28}^{4-}$ decavanadate-like precipitatum. Since hydrolysis is greatly increased at higher temperatures, the acidification in hydrophilic colloids surrounding hydrophobic particles and aggregations is also increased (Fig. 4), producing a red–brown precipitate of the orange colloidal system. During precipitation, the aggregations are decomposed by thermally forced hydrolysis (see Equations 6 and 10), and the liberated VO_3^- anions rapidly transform into decavanadate-type complexes (Equation 11) :

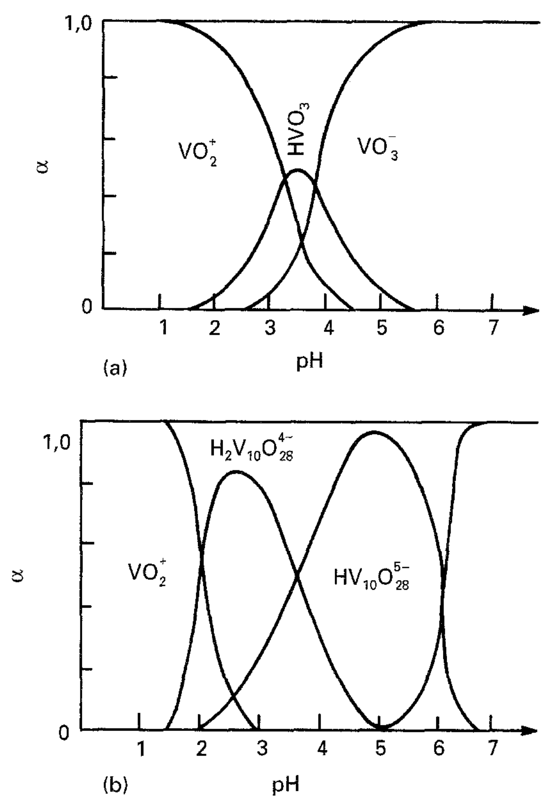

Figure 10 Relative distribution of vanadate species in: (a) small concentrated solution (10^{-5} mol [V] l^{-1}) after [17] and [15]) and (b) high concentrated solution (10^{-2}mol [V] l^{-1}) (after [29]).

$$10VO_3^- + mH_2O \leftrightarrows H_{(1+n)}V_{10}O_{28}^{(5-n)} + k_2H^+ + l_2(OH)^- \quad 0 \le n \le 1 \qquad (11)$$

Literature data show that these reactions are complete in two or three steps (reactions 4, 10 and 11 in Table II) and have reversible characteristics. However, in these cases, previous polymerization (monomer –trimer) is required for transformation into decavanadates. Since the colloidal structures possess similar character with polymerized $V_3O_9^{3-}$ or $V_4O_{12}^{4-}$ species, additional polymerization is not necessary at higher pHs (Fig. 9).

In this case the actual vanadyl anion composition is shifted from point 1 to point 2 of Fig. 9, in connection with the change of pH values at higher temperatures (Fig. 4). Point 1 represents (qualitatively) the anion composition of the original orange colloidal system; point 2 denotes the red–brown precipitate composition.

$HV_{10}O_{28}^{5-}$ decavanadate anion complexes can be formed by long-term ball-mill mixing. In this case the pH does not decrease, but increases slightly from 3.7 to 4.3 (Fig. 3). In hydrophilic colloidal media the mechanically-forced dissociation induces changes in the concentration and type of vanadyl anions, which affects the hydrophobic aggregation system and produces the VO_3^- anion. These species (similarly to the above mentioned precipitation process) transform into the $HV_{10}O_{28}^{5-}$ decavanadate anion (see point 3 in Fig. 9). The two types of decavanadate anions can be dissociated by reaction 9 in Table II. During both dissociations of orange aggregations the $Y_2O_{3-p}(OH)_p^{p+}$ species should exist, proved by presence of Y_2O_3 in the red–brown powder (see Fig. 5b and EDS observations). The major part of these species with decavanadate anions form the red–brown aggregation and the red–brown precipitation, as generally described by Equation 12. The minority of $Y_2O_{3-p}(OH)_p^{p+}$ species can further hydrolyse and form YVO_4 by Equation 13 and 14, while they form large size aggregations or precipitates by Equation 12. This is proved by obtained YVO_4 in the red–brown mixture (Fig. 5b). The large size decavanadate-like aggregations can generally be described by Equation 12:

$$Y_2O_{3-p}(OH)_p^{p+} + H_{(1+n)}V_{10}O_{28}^{(5-n)-} + yH_2O \rightarrow$$
$$Y_2O_{3-p}(OH)_p^{p+} \cdot H_{(1+n)}V_{10}O_{28}^{(5-n)-} \cdot yH_2O$$
$$0 \leq n \leq 1; \quad 0 \leq p \leq 3 \qquad (12)$$

This hydrophobic agglomeration is amorphous and dissociates very easily into species of Equation 13 with different p', n' ionization characters.

$$Y_2O_{3-p}(OH)_p^{p+} \cdot H_{(1+n)} V_{10}O_{28}^{(5-n)-} \cdot yH_2O$$
$$\leftrightarrows Y_2O_{3-p'}(OH)_{p'}^{p'+} + H_{(1+n')}V_{10}O_{28}^{(5-n')-} + k_3H^+$$
$$+ l_3(OH)^- \qquad 0 \leq (n, n') \leq 1;$$
$$0 \leq (p, p') \leq 3; \; n \neq n'; \; p \neq p' \qquad (13)$$

The decavanadate system is a mixture of $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ complex anions at pH ca. 4, as seen in Fig. 10b, and its statistically intermediate ionization stage is characterized by introduction of an n factor. Subsequently, the hydrolysed species of the red–brown mixture react to YVO_4 by Equation 14 producing irreversible chemical bonds of this compound.

$$5Y_2O_{3-p'}(OH)_{p'}^{p'+} + H_{(1+n')}V_{10}O_{28}^{(5-n')-} \rightarrow 10YVO_4$$
$$+ k_4H^+ + l_4(OH)^- \qquad (14)$$

During hydrolysation of decavanadate-type aggregations the pH value is < 6, which means limited, or no, chance for the presence of $V_3O_9^{3-}$, HVO_4^{2-}, or $V_{10}O_{28}^{6-}$ anions in the mixture while the system transforms into YVO_4.

Since both colloidal systems (orange and red–brown) and precipitation (red–brown) cannot return to the starting oxides or the previous colloidal system, the special modified dissociation processes described by Equations 6, 10 and 13 can be assumed. These dissociations result from the relatively high energy of hydrophobic bonds between different species, which was previously provided for adhesion by an intensive mixing (shear–flocculation) process. The large energy barrier can prevent the reversibility of aggregate formations (Equations 4, 9 and 12) and modify their dissociation behaviours. Equations 6, 10 and 13 give some possible descriptions for these modifications. Since protonized Y_2O_3 (Equation 3) can be reversed, during the YVO_4 reaction (Equation 8 and 14) process a small amount of the $Y_2O_{3-p}(OH)_p^{p+}$ species will not further hydrolyse into $Y_2O_2^{2+}$ (Equation 7) or $Y_2O_{3-p'}(OH)_{p'}^{p'+}$ but return to the original Y_2O_3 oxide form, which was observed in the XRD spectra (Fig. 5c). This unwanted part can be eliminated by accelerated mixing of the diluted red–brown colloid due to its intensive hydrolysis (Fig. 6). Short-term calcining processes can also perfectly eliminate it as seen in Fig. 5d. The accelerated mixing of the diluted red–brown colloidal system, in addition to elimination of the Y_2O_3 excess phases, give an excellent chance to react YVO_4 at room temperature.

By comparing the present technique with previous aqueous solution techniques (see Section 1), it can be established that this method is chemically simpler and more pure, since it does not utilize chemical reagents for YVO_4 formation other than V_2O_5, Y_2O_3 and H_2O; consequently, extraneous compounds and impurities are not formed as in the previous techniques. Since this preparation technique utilizes the special colloidal and hydrolysing character of V_2O_5 in aqueous solution [30], it is expected that it can be successfully applied to the preparation of other orthovanadates (especially rare earth orthovanadates, e.g. $ReVO_4$) from $V_2O_5 + A_2O_3$ aqueous solutions. Similarly, this hydrolysed colloid reaction technique can be successfully applied to orthophosphate (YPO_4) and orthophosphate–vanadate solid–solution systems [44]. It is also expected that the above described HCR technique, developed in the ball-mill system, can successfully be applied in special colloid-mill systems.

4. Conclusions

The following conclusions can be drawn from this work:

1. YVO_4 powder can be prepared by the hydrolysed colloid reaction (HCR) technique from $Y_2O_3 + V_2O_5 + H_2O$ non-ideal colloidal aqueous mixtures at low temperatures (25–95 °C) and atmospheric pressure.
2. The semi-hydrophobic colloidal structure can modify the dissociation mechanism which, on the one hand, prevents the system returning to its starting oxides and, on the other hand, gives a suitable ionic environment to realize the YVO_4 reaction by a simple hydrolysis process.
3. Two types of metastable, intermediate colloidal mixtures can be obtained with different mixing times which hydrolyse into the YVO_4 phase.
4. The slightly metastable orange mixture, containing metavanadate-type aggregations, precipitates into the more metastable decavanadate-type precipitation at 80 °C, pH 2.5, which rapidly hydrolyses toward YVO_4 at this temperature.
5. A diluted decavanadate-type red–brown colloidal system can transform into YVO_4 at room temperature due to an intensive mixing procedure.
6. Average particle size YVO_4 powder (0.1–0.3 μm) was prepared by the above described technique.

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