CERAMICS — Silikáty *34*, s. 61—67 (1990)

SYNTHESIS OF COBALT-BASED CERAMIC PIGMENTS FROM INDUSTRIAL WASTE MATERIAL

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Received 7. 12. 1988

The possibility of synthetizing cobalt pigments from a waste sediment from hydrometallurgical production of cadmium metal was studied. For the sake of comparison a parallel synthesis was made with the use of Co_3O_4, *prepared from* $Co(NO_3)_2 . 6 H_2O$ *of A.R. quality. In the synthesis of* $CoAl_2O_4$ *the influence of the molar ratio of reactants, temperature as well as the time of synthesis on the quality of the pigments obtained was studied. The process of the synthesis was described mathematically by linear and non-linear models in the temperature region of 1000 — 1200 °C in order to determine the effect of the process parameters on the reaction of spinel formation.*

INTRODUCTION

Because of the attractiveness and high temperature stability of the ceramic decors they produce, cobalt pigments are very expensive and sought-for materials. They are used for colouring ceramic glazes in amounts from 2 to 6 wt. % The colours of the pigments differ in dependence on the elements they contain, for instance green (Co and Cr), blue (Co, Al, Zn, Zr, Si and Cr), pink (Co, Si, P) or brown and black (Co, Cr, Ni, Fe and Mn).

In the present study the authors investigated the possibility of synthetising the cobalt pigments from waste sediments which are a by-product of hydrometallurgical production of cadmium metal. In industrial production of cadmium metal, significant quantities of cobalt concentrate with an average content of 8 wt. % of cobalt are obtained.

EXPERIMENTAL

To prepare the experimental materials, the waste sediment was first dissolved in sulphuric acid. In this way the cobalt was dissolved as $CoSO_4$ and the remaining ferrous compounds were oxidized and precipitated with $Ca(OH)_2$ as hydroxides. The sulphates of copper and cadmium were separated from the warm solution by so-called cementation with the use of zinc sheet metal. The Co^{2+} ions were

Table I

The content of impurities in cobalt hydroxide obtained from waste

impurity	Ni	Zn	Cd	Cu	Fe	Sb	Chlorides	Sulphates
wt. %	0.54	0.95	0.13	0.18	0.016	0.18	0.32	0.45

oxidized by NaOCl, precipitated as hydroxide and separated by filtration. The impurities present in the cobalt hydroxide obtained are listed in Table I. For synthesis of the pigments beside cobalt hydroxide, powdered α-Al_2O_3 from Kidričevo, Yugoslavia (with the content of Na_2O 0.4 wt. %, SiO_2 0.025 wt. % and Fe_2O_3 0.04 wt. %) and powdered ZnO (produced by "Zorka" Šabac, Yugoslavia) of A. R. quality were used. Parallel experiments were made with Co_3O_4 obtained from $Co(NO_3)_2 . 6 H_2O$ (Merck) of A. R. quality. X-ray analysis showed that the cobalt hydroxide obtained from the waste material was in the form of the mineral heterogenite, CoO(OH).

The starting material $Co(NO_3)_2 . 6 H_2O$ was heated to 300 °C in order to decompose it according to the reactions

$$Co(NO_3)_2 . 6 H_2O \rightarrow Co(NO_3)_2 + 6 H_2O \ (t = 50—233 \ °C) \quad (1)$$

$$Co(NO_3)_2 \rightarrow 1/3 \ Co_3O_4 + 2 NO_2 + 1/3 \ O_2 \ (t = 233—280 \ °C) \quad (2)$$

The composition of the reaction mixtures for the synthesis of cobalt aluminates is given in Table II.

Table II

The composition of reaction mixtures for synthesis of cobalt pigments

Mixture number	t. % of component in the reaction mixture				Molar ratio
	Al_2O_3	CoO(OH)	Co_3O_4	ZnO	Al_2O_3 : CoO
1	52.58	47.42	—	—	1 : 1
2	68.92	31.08	—	—	2 : 1
3	76.89	23.11	—	—	3 : 1
4	60.0	—	21.42*	20.0	
5	60.0	24.53*	—	20.0	

*) calculated as CoO

Heat treatment of the samples

The dry reaction mixtures were homogenized in a ball mill for 1 hour. The so-called flash ignition firing was used in order to obtain finely dispersed powders. According to the literature [1], it is thus possible to prevent the reaction mixture from sintering so that the final product of synthesis need not be ground.

Because the literature data [2, 3] indicated that a change of atmosphere from oxygen to nitrogen had no significant influence on the reaction kinetics, the heat treatment was carried out with air in free access.

Reaction course in the system CoO—Al_2O_3

In order to determine the influence of the process parameters in the synthesis of cobalt aluminates from waste CoO(OH), the method of full factor experiment according to Luri [4] was applied in the case of reaction mixture 1 from Table II. As the response function, the content of unreacted CoO was determined in the samples treated for certain time intervals at the selected temperatures. The content

of unreacted Co^{2+} ions was determined in solutions obtained after the dissolution of samples in warm (1 : 1) HCl by atomic absorption (Perkin Elmer Apparatus, wavelength 240.7 nm). The determinations were made at two points of each sample. The results are given in Table III.

Table III

The content of unreacted Co^{2+} in the reaction mixtures of CoO(OH) and Al_2O_3 heated at different temperatures in air

Temperature (°C)	Molar ratio Al_2O_3 : CoO	Time of treatment (h)	Uncreacted Co^{2+} (wt. %) Probe I	Probe II
1000	1 : 1	2.0	14.56	15.43
		4.0	12.39	10.66
		6.0	8.44	9.11
1100	1 : 1	2.0	2.38	2.17
		4.0	2.01	1.90
		6.0	1.49	1.62
1200	1 : 1	2.0	0.67	0.67
		4.0	1.67	0.90
		6.0	0.50	0.87
1300	2 : 1	4.0	0.03	—
	3 : 1	4.0	0.004	—

MATHEMATICAL TREATMENT OF THE EXPERIMENTAL DATA

The modelling of the process of synthesis was performed according to the plan of experiments given in Fig. 1. As a zero level the temperature of 1100 °C and the time of 4 hours was used. The interval of the temperature change was 100 °C,

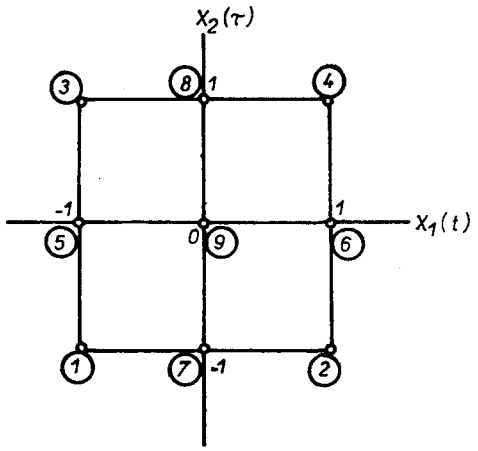

Fig. 1. The plan of experiment for the modelling of the process.

Table IV

Central orthogonal plan of the second order (k = 2) and mean values of the response function (the amount of unreacted Co^{2+})

Number of experiment	Coding values of variable					Response function y		
	x_1	x_2	$(x_1^2 - 2/3)$	$(x_2^2 - 2/3)$	x_1x_2	y_1	y_2	y_{mean}
1	−1	−1	1/3	1/3	+1	14.56	15.43	14.99
2	+1	−1	1/3	1/3	−1	0.67	0.67	0.67
3	−1	+1	1/3	1/3	−1	8.44	9.11	8.77
4	+1	+1	1/3	1/3	+1	0.50	0.87	0.68
5	−1	0	1/3	−2/3	0	12.39	10.66	11.52
6	+1	0	1/3	−2/3	0	1.16	0.90	1.03
7	0	−1	−2/3	1/3	0	2.38	2.17	2.27
8	0	+1	−2/3	1/3	0	1.49	1.62	1.55
9 (zero point)	0	0	−2/3	−2/3	0	2.01	1.90	1.95

Table V

Check of the models obtained by comparing the calculated and the experimental values

Experimental conditions		The amount of unreacted Co^{2+} Values calculated by means of models		(wt. %) Experimental (mean values)
x_1	x_2	Linear	Non-linear	
−1	−1	13.43	14.35	14.99
	0	11.88	11.58	11.52
	+1	10.33	8.81	8.77
0	−1	7.83	2.85	2.27
	0	6.28	1.55	1.95
	+1	4.73	0.54	1.55
+1	−1	2.23	0.30	0.67
	0	0.67	0.62	1.03
	+1	0.87	0.95	0.68

and that of the time change was 2 hours. For the experiment of type 2^2, the following equation of regression was obtained:

$$y = 6.278 - 5.604x_1 - 1.553x_2 + 1.558x_1x_2 \qquad (3)$$

where y is the cooling value of the response function (the amount of unreacted cobalt), x_1 is the temperature and x_2 is the time of reaction.

The reproducibility test, according to Kohern, showed the experiment to be well reproducible. However, the test for model adequacy according to Fisher's criterion indicated that the model was not adequate. The central orthogonal plan for the second order ($k = 2$), presented in Table IV, was therefore applied. In this way the non-linear model represented by the following equation was obtained:

$$y = 4.65 - 5.48x_1 - 1.22x_2 + 1.55x_1x_2 + 4.35(x_1^2 - \varphi), \quad (4)$$

$$\varphi = \sqrt{\frac{2k}{n}}, \quad (5)$$

where n is the number of experiments in the plan ($n = 9$ in this case). All the coefficients in equation (4) are significant according to Student's criterion. It is obvious that the effect of temperature on reducing the amount of unreacted CoO is more expressive than that of time. For this reason the pigments were synthetized at 1300 °C for 4 hours.

A comparison of the calculated values from both models and the experimental values is given in Table V. On the basis of these data it is obvious that the agreement between the calculated and the experimental values was better in the case of the non-linear model.

More experiments (at least fifteen) would be required for complete modelling of the synthesis process.

APPLICATION OF THE SYNTHETIZED PIGMENTS

The pigments obtained were applied on industrial scale in glazes for ceramic tiles in amounts of 3 wt. % in the Zorka ceramic tile works at Šabac. It was shown that

— the temperature changes under industrial conditions had no effect on the colour of glazed tiles,
— the atmosphere in the kiln had no effect on the stability of the pigments; they are stable in oxidating and slightly reducing atmospheres, and
— the composition of the industrial glaze and stirrers did not affect the thermal stability nor the colouring power of the pigments.

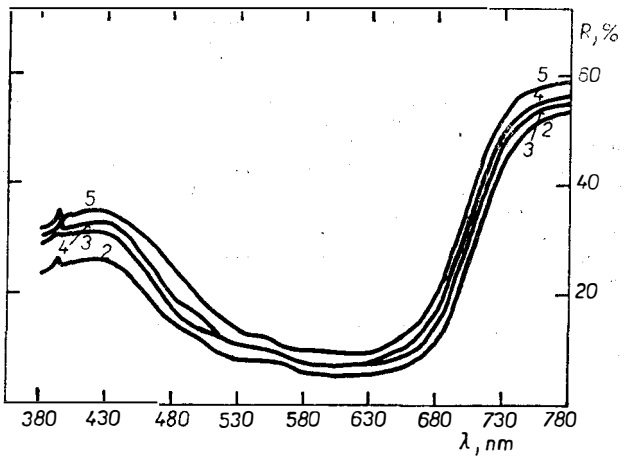

Fig. 2. Reflection curves of blue pigments, Composition of pigments: 2 — 68.92 % Al_2O_3, 31.08 % CoO(OH). 3 — 76.89 % Al_2O_3, 23.11 % CoO(OH). 4 — 60.00 % Al_2O_3, 20.00 % ZnO, 21.42 % Co_3O_4. 5 — 60.00 % Al_2O_3, 20.00 % ZnO, 24.53 % CoO(OH)**
* — *calculated as* CoO

Pigments synthetized from pure Co_3O_4 obtained from $Co(NO_3)_2 . 6 H_2O$ of A.R. quality were heated under the same conditions (1200 °C, 4 hours) as the pigments of the same compostion (mixtures 4 and 5 in Table II) based on the waste CoO(OH). Their optical characteristics are given in Fig. 2; there is no significant difference between the two.

CONCLUSION

On the basis of experimental results it can be concluded that

— the impurities present in CoO(OH) obtained from the waste sediment probably increase the reaction rate of cobalt aluminate formation,

— a change in the Al_2O_3: CoO molar ratio from 1 to 3 caused the colour shade to change to lighter blue tones because in this case the amount of unreacted Al_2O_3 was greater. The content of unreacted Co^{2+} was negligible (Table III),

— the pigments synthetized from waste CoO(OH) can be successfully applied in glazes for ceramic tiles under industrial conditions.

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SYNTÉZA KERAMICKÝCH PIGMENTŮ NA BÁZI KOBALTU Z PRŮMYSLOVÉHO ODPADU

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Cílem práce bylo ověřit možnost syntézy kobaltových pigmentů z kalů, které odpadají při hydrometalurgické výrobě kovového kobaltu. Nejprve byl tento odpadní materiál charakterizován chemickými a mineralogickými metodami.

V soustavě $CoO—Al_2O_3$ byla syntetizována řada pigmentů o různých barvách. Pro srovnání byly paralelně připraveny pigmenty z výchozího Co_3O_4, získaného z $Co(NO_3)_2 . 6 H_2O$ p. a. Při syntéze $CoAl_2O_4$ byl sledován vliv molárního poměru výchozích látek, teploty a času na kvalitu získaných pigmentů. Proces syntézy byl popsán matematicky v teplotní oblasti 1000—1200 °C, aby se určil vliv parametrů procesu na reakci vzniku spinelu.

Laboratorně připravené pigmenty byly použity v průmyslových podmínkách do glazur pro keramické dlaždice v množství 3 % hm. V tomto případě se ukázalo, že optická charakteristika pigmentů připravených z odpadu a z chemikálií o čistotě p. a. je téměř shodná. Na základě toho je možno shrnout, že odpad lze úspěšně použít pro výrobu řady keramických pigmentů na bázi sloučenin kobaltu.

Obr. 1. Plán experimentů pro modelování procesu.

Obr. 2. Křivky odraznosti modrých pigmentů. Složení pigmentů: 2 — 68,92 % Al_2O_3, 31,08 % Co(OH). *3 — 76,89* % Al_2O_3, *23,11* % Co(OH). *4 — 60,00* % Al_2O_3, *20,00* % ZnO, *21,4* % Co_3O_4*. *5 — 60,00* % Al_2O_3, *20,00* % ZnO, 24,53 % CoO(OH)*
* — *přepočteno na* CoO.

Synthesis of Cobalt-Based Ceramic Pigments from Industrial Waste Material

СИНТЕЗ КЕРАМИЧЕСКИХ ПИГМЕНТОВ НА БАЗЕ КОБАЛЬТА ИЗ ПРОМЫШЛЕННЫХ ОТХОДОВ

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Целью приводимой работы является исследование возможности синтеза кобальтовых пигментов из шламов, отходящих при гидрометаллургическом производстве металлического кобальта. Прежде всего был установлен состав отходов с помощью химических и минералогических методов.

В составе CoO — Al_2O_3 был синтетизирован ряд пигментов разного цвета. Для сопоставления были параллельно приготовлены пигменты из исходного Co_3O_4, полученного из $Co(NO_3)_2 . 6 H_2O$ д. а. При синтезе $CoAl_2O_4$ исследовали влияние молярного отношения исходных веществ, температуры и времени на качество полученных пигментов. Процесс синтеза описывали математически в пределах температур 1000—1200 °C с целью установить влияние параметров процесса на реакцию образования шпинели.

Приготовленные лабораторным путем пигменты использовали в промышленных условиях для приготовления глазурей, предназначенных для керамических плиток в количестве 3 % по весу. В данном случае было доказано, что оптическая характеристика пигментов, приготовленных из отходов и химических веществ чистотой д. а. почти одинакова. На основании того можно выводить, что отходы можно с успехом использовать для производства ряда керамических пигментов, получаемых на базе соединений кобальта.

Рис. 1. План экспериментов для моделирования процесса.

Рис. 2. Кривые отражения синих пигментов. Состав пигментов: 2 — 68,92 % Al_2O_3, *31,08 %* Co(OH), *3 — 76,89 %* Al_2O_3, *23,11 %* Co(OH), *4 — 60,00 %* Al_2O_3, *20,00 %* ZnO, *21,4 %* Co_3O_4*, *5 — 60,00 %* Al_2O_3, *20,00 %* ZnO, *24,53 %* Co(OH)* * *— при пересчете на* CoO.

FEUERFESTBAU. STOFFE–KONSTRUKTION–AUSFÜHRUNG (Žárovzdorné stavby. Materiály–konstrukce–provedení); redakce Německá společnost pro stavbu žárovzdorných agregátů a komínů, 303 stran, 98 DM, Vulkan Verlag, Essen 1987.

Po delší pause vyplněné pouze některými překlady z japonské odborné literatury do ruštiny, objevuje se kniha německých specialistů v oboru stavby žárovzdorných agregátů. Zahrnuje poslední poznatky a využití progresivních materiálů, včetně lehčených žáromonolitů a vláken.

V prvé části je uveden stručný přehled žárovzdorných staviv s důrazem na jejich základní vlastnosti. Preferovány jsou především tepelně izolační a též řada pomocných materiálů, jako jsou např. tmely, nátěry, malty, směsi pro spáry apod.

Další kapitola se týká konstrukce agregátů s využitím základních druhů materiálů, jako jsou tvarové hutné, tvarové tepelně izolační, netvarové a vláknité materiály. Součástí této kapitoly jsou též poznatky týkající se přestupu a prostupu tepla a tepelně technické výpočty. Závěr kapitoly tvoří statické výpočty při působení teploty.

Třetí hlavní část je věnována provedení stavebních úkonů. Dělení je opět provedeno podle základních druhů žárovzdorných staviv s ohledem na různé typy agregátů resp. jejich částí (rotační pece, klenby, oblouky apod.).

Závěr tvoří stručné pasáže o uvádění do provozu, tj. o sušení, temperování a odtemperování pecních agregátů a příslušných normách.

Kniha je výbornou příručkou především pro konstruktéry a stavitele vysokoteplotních agregátů, bude však jistě užitečná i pro posluchače a pedagogy vysokých škol příslušných oborů.

J. Kutzendörfer