

Původní práce

THE EFFECT OF WATER VAPOUR ON THE RATE OF SURFACE DIFFUSION ON CALCIUM SILICATES

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A vacuum-deposited SrO layer on defined surfaces of α -wollastonite and α' -dicalcium silicate monocrystals behaves as a store of surface diffusion during tempering at $T = 1150$ — 1350 K. The diffusion coefficients calculated from the SrO surface density profiles, established by X-ray microanalysis, are significantly higher with specimens tempered in water vapour than with those tempered in dry air. The analogy with CaO allows to assume that surface diffusion, accelerated by the water vapour in the furnace atmosphere, takes an important part in the mechanism of calcium silicates formation.

INTRODUCTION

The accelerating effect of water vapour on the reactions in the system CaO—SiO₂ has been known for a long time [1]. The effect was recently studied in detail by Burte and Nicholson [2], Jesenák and Hrabě [3], [4] and by Kovár [5].

At 1573 K the transport of CaO through the gaseous phase, caused by the presence of water vapour in the furnace atmosphere, [6] was observed. The accelerating effect of water vapour in the synthesis of calcium silicates was likewise observed in the lower temperature region [7]; however, in this instance no transport through the gaseous phase was discernible [6]. The present authors assume that the effect is based on the acceleration of calcium transport by surface diffusion over the surface of polycrystalline reaction products, i.e. wollastonite and dicalcium silicate.

The present paper has the aim to elucidate the mechanism of the effect in question over the temperature range of 1150 to 1350 K by comparing the rates of the diffusion processes.

The problem involved a study of the surface diffusion of SrO on the monocrystals of α -wollastonite and β -dicalcium silicate in the course of heating up the specimens in a water vapour atmosphere. The rate of diffusion was compared with that in the medium of dry air. The SrO was used as an analog of CaO to obtain a more distinct ratio of the signal to noise in the microprobe measurements.

EXPERIMENTAL

The monocrystals of α -wollastonite and β -dicalcium silicate were prepared from high-temperature melts of calcium chloride according to [8]. The SrO was vacuum-deposited in the form of bands 40 μm in width onto the (0001) pseudohexagonal basal plane of α -wollastonite or onto the (011) pseudorhombic prismatic plane of

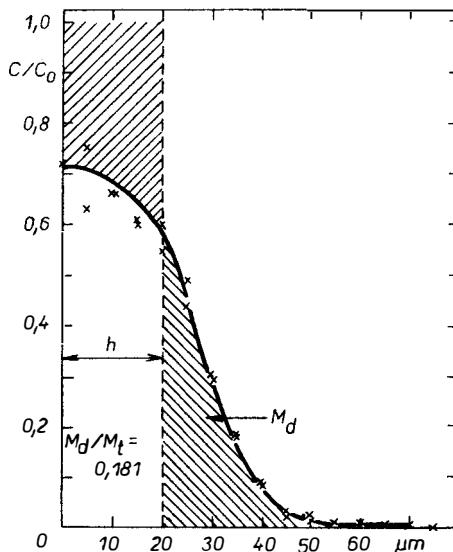


Fig. 4. Relative surface density profile (C/C_0) of SrO on α -wollastonite after tempering for 3600 s at 1250 K in air, including the proportion of SrO diffused from the originally deposited region (h); (X — experimental values, curve path through the experimental points).

Table I

Experimental values of relative surface density of SrO, $C_x = 100C/C_0$ on α -wollastonite in terms of the distance ($x/\mu\text{m}$) from the symmetry plane of the system

In water vapour					In air		
1150 K 7200 s	1200 K 7200 s	1250 K 1800 s	1300 K 3600 s	1350 K 3600 s	1250 K 3600 s	1300 K 3600 s	1350 K 3600 s
$x \ C_x$							
0 73	0 62	3 62	0 40	3 50	0 72	2 55	0 100
5 82	5 52	8 65	5 42	8 49	5 69	7 59	5 99
10 80	10 36	13 62	10 41	13 51	10 66	12 60	10 88
15 77	15 56	18 61	15 41	18 52	15 61	17 59	15 85
20 60	20 58	23 57	20 40	23 54	20 58	22 51	20 40
25 35	25 54	28 40	25 38	28 50	25 46	27 38	25 24
30 12	30 44	33 33	30 37	33 40	30 30	32 39	30 10
35 1	35 40	38 15	35 35	38 26	35 18	37 22	35 5
	40 14	43 35	40 32	43 13	40 8	42 11	40 3
	45 8	48 1	45 23	48 5	45 3	47 6	45 2
	50 2	53 1	50 15	53 3	50 2	52 3	50 1
	55 0.5	58 0.5	55 11	58 2	55 1	57 2	55 0.5
			60 7	63 1	60 0.5	62 2	60 0.5
			65 5	68 1		67 1	
			70 4	73 0.5		72 0.5	
			75 3				
			80 2				
			85 0.5				

β -dicalcium silicate in the $\langle 011 \rangle$ direction (Fig. 1). The specimens were tempered at 1150 to 1350 K in dry air (water vapour tension below 0.8 Pa), and in water vapour in a controlled tubular furnace with a linear rate of flow of the atmosphere of 2 cm s^{-1} . The diffusion profiles were obtained by quadruple "STEP SCAN" microprobe measurement (JEOL JX-5A) perpendicularly to the direction of the bands using a step length of $x = 5 \mu\text{m}$ where each point was measured for 10 seconds. The SrO profiles obtained exhibited a relatively high noise level (cf. Figs. 1 through 3) so that the values were averaged, corrected for background and transferred into the positive semispace (Fig. 4). The pulse frequencies both measured and corrected (I) were considered to be proportional to the surface density of SrO (further C — concentration). All the concentration profiles were related to that of the originally deposited band with a maximum SrO concentration, C_0 . The half widths of the original SrO bands determined by calculation amounted to $19.8 \pm 0.2 \mu\text{m}$.

The results of the determinations are listed in Tables I and II.

Table II

Experimental values of the surface density of SrO, $C_x = 100 C/C_0$ on α' -dicalcium silicate in terms of the distance ($x/\mu\text{m}$) from the symmetry plane of the system

In water vapour		In air	
1300 K 3600 s		1300 K 3600 s	
x	C_x	x	C_x
0	32	2	54
10	23	12	51
20	28	22	92
30	24	32	30
40	18	42	16
50	13	52	8
60	10	62	5
70	8	72	3
80	7	82	2
90	7	92	2
100	6	102	1
110	6	112	1
120	6	122	0.5
130	5		
140	4		
150	3		
160	2		
170	1		
180	0.5		

DISCUSSION OF THE RESULTS

For the purpose of checking, the overall relative amount of SrO was determined in the specimens using numerical summation of the pulse frequencies measured, using the equation

$$M_t = k \sum_{i=1}^n I_i \Delta x \quad (1)$$

where k is a constant having the dimension [MTL⁻¹]. The distinct decrease of the M_t values observed with the specimens tempered at 1350 K was due to vaporization of some of the SrO.

In all the instances, the share of SrO diffused from the original region (M_d) and related to the total amount of SrO (M_t) was determined. The values of M_d/M_t obtained in this way are listed in Table III and clearly demonstrate the accelerating effect of water vapour on the surface diffusion of SrO.

Table III

The amounts of SrO diffused after 3600 s of tempering from the originally deposited region M_d/M_t and the diffusion coefficients calculated according to the store model

$\frac{T}{[K]}$	Atmosphere	M_d/M_t	D_s [m ² s ⁻¹]	Substrate
1150**)	H ₂ O	0.032	3.7×10^{-15}	$\alpha\text{-CaSiO}_3$
1200**)	H ₂ O	0.220	3.2×10^{-14}	(0001)
1250	H ₂ O air	0.290 0.181	5.6×10^{-14} 2.3×10^{-14}	
1300	H ₂ O air	0.373 0.278	1.6×10^{-13} 4.1×10^{-14}	
1350	H ₂ O air	0.336 0.025	7.7×10^{-14} 3.2×10^{-1}	
1300*	H ₂ O air	0.536 0.340	3.6×10^{-13} 6.7×10^{-15}	$\alpha'\text{-Ca}_2\text{SiO}_4$ (011)

*) The values at this temperature are not representative, as some of the deposit has vaporized.

**) Diffusion was not observed in dry air atmosphere.

To create a base for the diffusion mechanism and for the calculation of diffusion coefficients, the concentration profiles measured were compared with the concentration courses from various theoretical model conceptions. It was assumed that

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2}, \quad (2)$$

is valid, where the diffusion coefficient (D) is independent both of the concentration of the diffusing component as well as of the time.

The differential equation (2) was resolved for three models of the system in question using various initial and boundary conditions [9]. The optimum values of the diffusion coefficients for each model were obtained by the Simplex method and employed in the calculation of the theoretical concentration profiles according to equations (3), (4), (5).

When using the assumption that the SrO deposit is originally present in an infinitely thin band (the line model), the total amount (M) originally deposited at time $t = 0$ is concentrated in the line $x = 0$.

The course of concentration is then given by the following equation:

$$C_{(x, t)} = \frac{M}{(4\pi Dt)^{1/2}} \exp - \left(\frac{x^2}{4Dt} \right). \quad (3)$$

As shown by Figs. 5 and 6, this model does not adequately reproduce the concentration profiles measured.

In assuming that SrO was originally deposited in a band of $2h$ width, symmetrically to $x = 0$ (the band model), equation (2) yields the concentration course of SrO in the form

$$C = \frac{C_0}{2} \left[\operatorname{erf} \frac{h-x}{(4\pi Dt)^{1/2}} + \operatorname{erf} \frac{h+x}{(4\pi Dt)^{1/2}} \right]. \quad (4)$$

As indicated by the example in Figs. 5 and 6, our initial assumptions do not comply precisely with the experimental results.

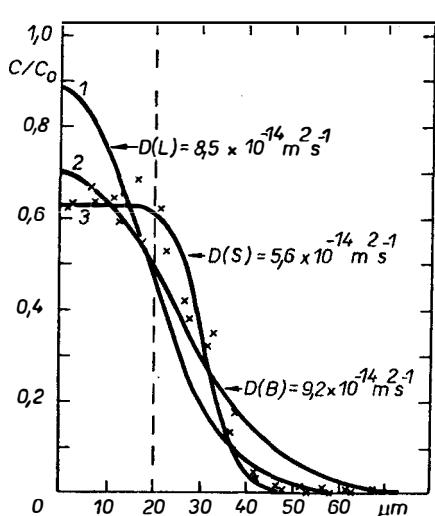


Fig. 5. Experimentally determined relative surface densities of SrO (X) after tempering the deposit on α -wollastonite for 1800 s at 1250 K in water vapour. Correlation of experimental values: 1 — line model, 2 — band model, 3 — store model, and the respective calculated values of diffusion coefficients (D_L , D_B , D_S).

Fig. 6. Experimentally determined surface densities of SrO (X) after tempering the deposit on α -wollastonite for 7200 s at 1350 K in water vapour. Correlation of the experimental values: D_L — from the line model, D_B — from the band model, D_S — from the store model.

It appears that the SrO deposit creates in the deposited bands a certain store which keeps its concentration on an approximately constant level at $x = h$. When thus using the conditions $x = h$, $t \geq 0$, $C = C_0$, the following solution holds true (store model):

$$C = C_0 \operatorname{erfc} \frac{x}{(4\pi Dt)^{1/2}}. \quad (5)$$

The examples shown in Figs. 5 and 6 indicate to a satisfactory agreement with the experimental results. The optimum values of the diffusion coefficients (D_S) calculated according to the equation (5) are listed in Tabel III.

A comparison of the individual models in question implies that
— the largest deviations from the experimental relationships are produced by the line model; the band model exhibits smaller deviations from the experimental

- relationships C vs. x ; however, these appear to be systematic. These two models are therefore unsuitable for describing the system;
- the store model reproduces well the course of the experimental results; however, following longer time of diffusion, the C_0 value decreases as a result of depletion of the deposit store.

The problems involved in the surface diffusion on calcium silicates have not so far been studied. The quantitative results of the present work should be evaluated while taking into account the initial assumptions, i.e.:

- the direct proportionality between the pulse frequency of the $\text{Sr}_{L-\alpha}$ radiation measured and the surface deposit density (C),
- that the SrO on the surface of calcium silicates behaves in the same way as CaO ,
- that the vaporization rate of SrO and the volume diffusion below 1350 K are negligible,
- that the directional anisotropy of surface diffusion on the α -wollastonite specimens had no significant effect.

In spite of these limitations, the following conclusions can be drawn on the basis of the results obtained:

- the surface heterodiffusion of Sr ions on α -wollastonite and on dicalcium silicate is accelerated significantly in the temperature range of 1150 to 1350 K in an atmosphere of water vapour compared to that of dry air,
- that the experimental arrangement employed can be most suitably interpreted by the "store diffusion model",
- that on the basis of the analogy of Ca and Sr ions it may be assumed that CaO behaves similarly in its surface diffusion on calcium silicates.

The results allow the following assumptions to be formulated:

- the formation of calcium silicates is determined by the mechanism of CaO diffusion on the surface of polycrystalline products,
- the mechanism of the accelerating effect of water vapour on the syntheses of calcium silicates from powdered mixtures at temperatures below 1300 K is based on influencing the surface diffusion of the Ca component through the polycrystalline layers of the products.

It should be taken into account that water vapour as well as other specific components of the atmosphere influence the rate of solid phase reactions even through their effect on the morphological structure of the product layer (thus likewise changing the size of the effective diffusion cross section), as well as by influencing the phase composition development of the products of reaction [7], i.e. the ratio of the product to the reaction semiproduct.

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The Effect of Water Vapour on the Rate of Surface Diffusion on Calcium Silicates

ŠTÚDIUM VPLYVU VODNEJ PARY NA POVRCHOVÝ DIFÚZIU NA KALCIUMSILIKÁTOCH

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Vplyv atmosféry výpalu na povrchovú difúziu SrO na monokryštáloch α -wollastonitu a α' -dikalciumsilikátu sa študoval pri teplotách 1150—1350 K. Na povrch monokryštálov kalciumsilikátov sa deponoval 40 μm široký pás SrO vákuovým naparením. Vzorky sa temperovali v priestoroch atmosférach suchého vzduchu a vodnej par. Profily povrchovej hustoty SrO (obr. 1—3) sa merali mikro-rtg analýzou a korelovali s troma modelmi difúznej sústavy (obr. 5 a 6). Difúzne koeficienty sa počítali z experimentálnych dát simplexovou metódou. Z výsledkov vyhodnotení difúznych koeficientov vyplýva, že vodná para výrazne urýchľuje povrchovú difúziu SrO na kalciumsilikátoch. Z analógie SrO a CaO sa predpokladá podobný efekt pri povrchovej difúzii CaO. Výsledok potvrzuje, že syntéza kalciumsilikátov v danej teplotnej oblasti z kremena a CaO resp. kalcitu je riadená mechanizmom transportu CaO difúziou po povrchu zrn polykryštálických produktov (CS a C₂S). Nakonko syntézy wollastonitu a dikalciumsilikátu sa urýchľujú tiež vplyvom vodnej par [1—5] a transport CaO cez plynnú fázu sa vylučuje pri teplotách pod 1250 K [6] možno vysvetliť záver, že mechanizmus tohto vplyvu je v urýchlení povrhovej difúzie CaO vplyvom H₂O v pecnej atmosfére.

Obr. 1. Pôvodný depozit vrstvy SrO na povrchu monokryštálu α -wollastonitu. Líniové profily: horná čiara — Ca_{Ka}; dolná čiara Sr_{Lx} (na kompozícii aj na čiare líniovej analýzy — snímanej s vysokou časovou konštantou — sa javí pás depozitu širší ako podľa presných „STEP SCAN“ analýz).

Obr. 2. Depozit vrstvy SrO na α -wollastonite po temperovaní 3600 s pri 1300 K vo vzduchu a líniový profil Sr_{Lx}.

Obr. 3. Depozit vrstvy SrO na α -wollastonite po temperovaní 3600 s pri 1300 K vo vodnej pare a líniový profil Sr_{Lx}.

Obr. 4. Profil relatívnej povrhovej hustoty (C/C₀) SrO na α -wollastonite po temperovaní 3600 s pri 1250 K vo vzduchu s vyznačením podielu SrO vydišudovaného z pôvodne deponovanej oblasti (h); (× — exp. hodnoty, krvka preložená exp. bodmi).

Obr. 5. Experimentálne stanovené relativejne povrhové hustoty SrO (×) po temperovaní depozitu na α -wollastonite 1800 s pri 1250 K vo vodnej pare. Korelacia experimentálnych hodnôt: 1 — čiarový model, 2 — pásový model, 3 — zásobníkový model, a príslušné vypočítané hodnoty difúznych koeficientov (D_L, D_B, D_s).

Obr. 6. Experimentálne stanovené povrhové hustoty SrO (×) po temperovaní depozitu na α -wollastonite 7200 s pri 1350 K vo vodnej pare. Korelacia experimentálnych hodnôt: D_L — z čiarového modelu, D_B — z pásového modelu, D_s — zo zásobníkového modelu.

ИССЛЕДОВАНИЕ ВЛИЯНИЯ ВОДЯНОГО ПАРА НА ПОВЕРХНОСТНУЮ ДИФУЗИЮ НА КАЛЬЦИУМСИЛИКАТАХ

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Исследовали влияние среды обжига на поверхностную диффузию SrO на монокристаллах α -волластонита и α' -дикальциумсиликата при температурах 1150—1350 K. На поверхности монокристаллов кальциумсиликатов выделялась полоса SrO шириной в 40 μm в результате вакуумного пропаривания. Образцы темперировали в проточных средах сухого воздуха и водяного пара. Профили поверхностной плотности SrO (рис. 1—3) измеряли с помощью микрорентгеновского анализа и коррелировали с тремя моделями диффузной системы (рис. 5 и 6). Диффузные коэффициенты рассчитали из экспериментальных данных с помощью метода симплекса. Из результатов оценки

диффузных коэффициентов следует, что водяной пар резко ускоряет поверхностную диффузию SrO на кальциумсиликатах. На основании аналогии SrO и CaO предполагается подобный эффект при поверхностной диффузии CaO. Результат показывает, что синтез кальциумсиликатов в данной температурной области из кварца и CaO или кальцита управляемся механизмом транспорта CaO диффузией по поверхности зерен поликристаллических продуктов (CS и C₂S). Так как синтезы волластонита и дикальциумсиликата ускоряются также под влиянием водяного пара [1—5] и транспорт CaO через газовую фазу выделяется при температурах ниже 1250 K [6], можно сделать вывод, что механизм данного влияния заключается в ускорении поверхностной диффузии CaO под действием H₂O в среде печи.

Рис. 1. Первоначальный остаток слоя SrO на поверхности монокристалла α-волластонита. Линейные профили: верхняя линия — Сака, нижняя линия — Sr_{TG} (как на композиции, так и на линии линейного анализа — проводимого с высокой константой времени — проявляется полоса остатка более высокой по сравнению с точными „STEP SCAN“ анализами).

Рис. 2. Остаток слоя SrO на α-волластоните после темперирования 3600 с при температуре 1300 K во воздухе и линейный профиль Sr_{TG}.

Рис. 3. Остаток слоя SrO на α-волластоните после темперирования 3600 с при температуре 1300 K во водяном паре и линейный профиль Sr_{TG}.

Рис. 4. Профили относительной поверхностной плотности (C/C₀) SrO на β-волластоните после темперирования 3600 с во воздухе с обозначением доли SrO, дифундирующего из первоначальной отложенной области (h); (X — экс. величины, кривая, проводимая через экс. точки).

Рис. 5. Установленные экспериментальным путем относительные поверхностные плотности SrO (X) после темперирования остатка на α-волластоните 1800 с при температуре 1250 K во водяном паре. Корреляция экспериментальных величин: 1 — линейная модель, 2 — полосовая модель, 3 — бункерная модель и соответствующие расчетные величины диффузных коэффициентов (D_L, D_B, D_s).

Рис. 6. Установленные экспериментальным путем поверхностные плотности SrO (X) после темперирования остатка на α-волластоните 7200 с при температуре 1350 K во водяном паре. Корреляция экспериментальных величин: D_L — из линейной модели, D_B — из полосовой модели, D_s — из бункерной модели.

DIESELOV MOTOR Z KERAMIKY. V rámci západoeurópskej dohody o výskume naprojektoval sa 500 ccm jednoválcový motor. Motor skonštruovali a vyskúšali v University College v Dubline, Írska republika. Valec a piest vyrobili z α-SiC v Carborundum Corp., Niagara Falls, USA.

Dôležitý je poznatok podstatného zníženia trenia piestu o válec. Plánuje sa konštrukcia 1 000 ccm jednoválcového motora. Cieľom výskumu je tiež vývoj skúšobných metod keramických materiálov pre dieselové motory.

Die Umschau No. 6, z 16. 3. 1983

I. Vojtaššák

SKELNÉ A KRYSTALICKÉ SYSTÉMY Z GELÚ: CHEMIE A TECHNICKÉ APLIKACE. H. Dislich/J. Non-Cryst. Solids 57, 371/1983).

Syntézy skel, sklokeramických a keramických materiálů metodou sol-gel bylo mnohokrát úspešně použito pro řešení výzkumných problémů. Dnes se této metody používá v mnoha obořech v technologickém měřítku. Je to především výroba preformy pro tažení komunikačních vláken, výroba dutých kuliček pro jaderné palivo, výroba nosičů katalyzátorů, hutných a dokonale homogenních víceoxidových povlaků na sklech aj. Přehled o těchto aplikacích a přednostech této nové techniky shrnuje výstižně uvedený článek.

Šatava

The Effect of Water Vapour on the Rate of Surface Diffusion on Calcium Silicates

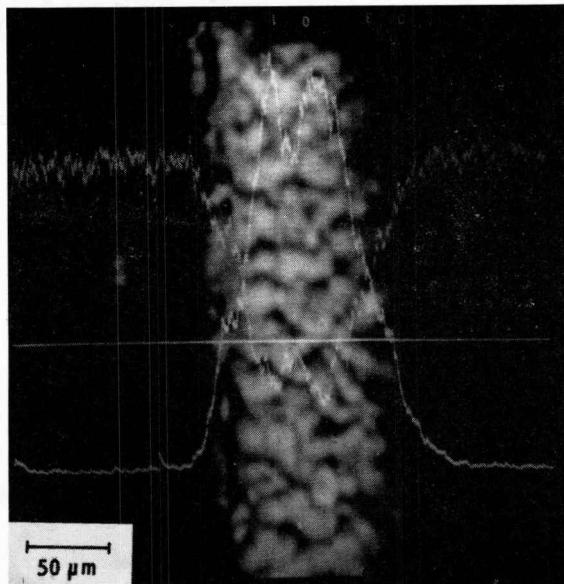


Fig. 1. Original deposit of the SrO layer on the surface of α -wollastonite monocrystal. The line profiles: top line — $\text{Ca}_{\text{K}\alpha}$; bottom line — $\text{Sr}_{\text{L}\alpha}$ (on the composition as well as on the line analysis pattern, scanned with a high time constant, the deposit band appears wider than according to the precise „STEP SCAN“ analyses).

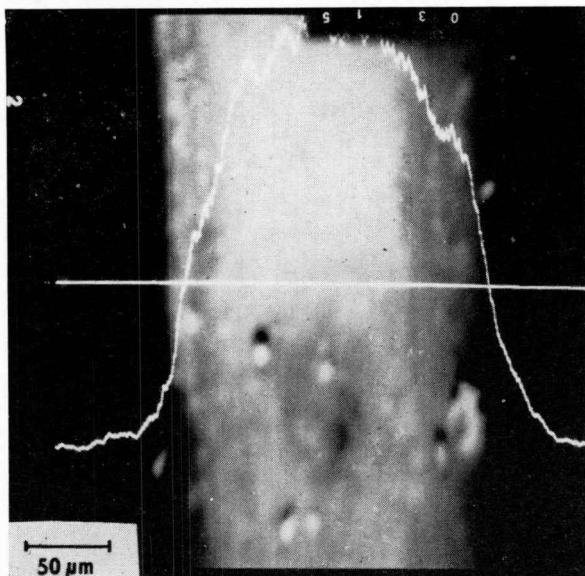


Fig. 2. Deposit of the SrO layer on α -wollastonite after tempering for 3600 s at 1300 K in air, and the $\text{Sr}_{\text{L}\alpha}$ line profile.

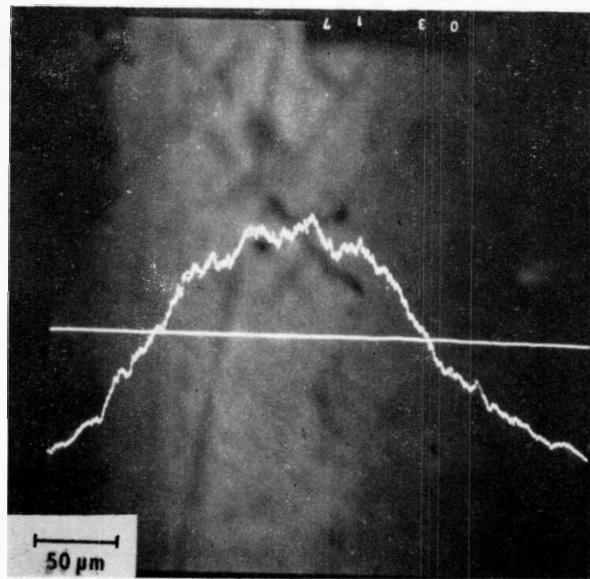


Fig. 3. Deposit of the SrO layer on α -wollastonite after tempering for 3600 s at 1300 K in water vapour, and the Sr_{Lα} line profile.