Původní práce

INTERACTIONS BETWEEN KAOLIN FIBRES AND CEMENT AT HIGH TEMPERATURES

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Plate materials composed of aluminosilikate ceramic fibres bonded with alumina or Portland cement with or without the addition of high-silica flue dust of an amorphous structure were heat treated at temperatures up to 1300 °C.

The specimens containing alumina cement and silica flue dust show upon heating to above 1100 °C the formation of anorthite and gehlenite besides CA phase. Analogically treated specimens without flue dust were found to contain only the original clinker minerals: CA, CA₂ and small quantities of C₁₂A₇. Specimens on the basis of Portland cement and flue dust contained a certain quantity of wollastonite after heating to temperatures above 800 °C and gehlenite after heating beyond 1000 °C, regardless of the presence of flue dust.

Ceramic fibres bonded with alumina and Portland cement and containing silica flue dust are more resistant to corrosion than fibres from the corresponding prepared without the addition of silica flue dust. The ceramic fibres were partly fused at 1300 °C.

INTRODUCTION

The utilization of thermal insulating materials containing ceramic fibres as micro-reinforcements has gained technical significance, especially as a consequence of the general shortage of fuels and energy.

Limited quantities of ceramic fibre materials are manufactured in Czechoslovakia (Termovit, Resistex) and their technology and applications abroad are covered by patents; they are described mainly in internal publications, so that relatively few references can be found in literature [1] — [5]. For this reison it was considered necessary to study the interactions between the fibres themselves and alumina or Portland cement at temperatures between 800 and 1 300 °C which represent the main application temperatures for the products in question.

The aim of the studies was to assess the viability of the production of cement bonded fibrous products and to investigate the possibility of reinforcing the surface of the plate in order to improve its abrasion resistance. Last but not least, the subject matter included the problems of manufacture of refractory concrete reinforced with refractory fibres. The latter application has recently gained great significance for local industrial applications.

EXPERIMENTAL

Starting materials

The experiments were carried out with Czechoslovak refractory fibres of the kaolin type with the trade name Resistex R 12, obtained from pilot plant production (SiO_2 — 55.18 %, Al_2O_3 — 42.86 %, Fe_2O_3 — 0.24 %, CaO — 0.20 %, MgO — 0.18 %,

ignition loss — 0.25 %, refractorines 1 680 °C, mean fibre thickness 4.5 μm, length index 8.0 cm, contents of grains larger than 0.5 mm — 3.3 %).

The high-alumina cement used in the experiments was Sécar 71 of French manufacture (in the early stages Sécar 250) which can be regarded as a standard material. Alumina cements are at present not yet manufactured in Czechoslovakia.
(SiO_2 — 0.36 %, Al_2O_3 + SiO_2 — 69.45 %, Fe_2O_3 — 0.41 %, CaO — 28.14 %, MgO — 0.87 %, ignition loss 0.27 %, refractoriness 1 545 °C.)

Portland cement of the PC 400 type from the Hranice Cement Plant (ČSSR) had the following characteristics and composition: insoluble residue 0.04 %, ignition loss 0.76 %, SiO_2 — 20.14 %, Al_2O_3 — 5.91 %, Fe_2O_3 — 3.25 %, TiO_2 — 0.27 %, CaO — 65.02 %, MgO — 1.22 %, K_2O — 0.67 %, Na_2O — 0.16 %, SO_3 — 2.44 %. Cements of this type are employed locally for the manufacture of refractory concretes for temperatures up to 1 100 °C.

As microfiller for the Portland cement was used silica flue dust of an amorphous structure from the Mníšek pod Brdy Works. (SiO_2 — 97.27 %, Al_2O_3 — 0.51 %, Fe_2O_3 — 0.10 %, TiO_2 — 0.01 %, CaO — 0.54 %, MgO — 0.37 %, K_2O — 0.40 %, Na_2O — 0.06 %, moisture content 0.46 %, ignition loss 0.68 %, bulk density 245 kg . m^{-3}.)

Preparation of test specimens

The specimens were prepared from the Resistex fibres by lamination and subsequent filling with the cement suspension with or without the addition of silica flue dust. Specimens with a thickness of approx. 40 mm were prepared from the individual about 5 mm thick Resistex layers. The fibre — cement weight ratio was 75 parts to 425 parts; when flue dust was introduced, the fibre — cement — flue dust ratio was 65 parts to 250 parts to 100 parts. The water — cement ratio of the material with and without the flue dust was 2.0 and 0.50, respectively. The bulk density of the material with and without the flue dust was 500 kg . m^{-3} and 700 kg . m^{-3}, respectively.

With regard to the fact that no commercial products were available, the samples were prepared in a way which was considered suitable for technical applications.

The specimens were treated in a way similar to the testing of cements, i.e. the specimens with alumina cement were stored a fortnight and those with Portland cement 7 days in an environment with a relative humidity of 100 %. After this period the specimens were dried and heat treated in an oxidizing atmosphere (Superkantal furnace) at the following temperatures: 1 100 °C, 1 200 °C and 1 300 °C (alumina cement), and 800 °C, 1 000 °C, 1 100 °C, 1 200 °C and 1 300 °C (Portland cement). The length of the isothermal holding period at the maximum temperature was 2 hours.

Methods employed

Besides the classical chemical methods, the main phase composition was determined by means of an X-ray diffractograph with a Philips proportional counter.

The microstructure of the heat treated specimens was studies by the STEREO-SCAN 2A scanning electron microscope (Cambridge Scientific Instruments, Cambridge, England) which provides a direct magnification from ×20 to ×100 000 with a resolution of about 100 Å. The microstructure was studied on a fresh fracture surface of the specimen which was vacuum coated with a thin gold layer.

DISCUSSION

Phase composition

Specimens with alumina cements

The main phase of the specimens after the hydration of the cement was Al_2O_3 . $3 H_2O$ (gibbsite) together with a smaller quantity of C_3AH_6, CAH_{10} and possibly $C_3A . CaCO_3 . 12 H_2O$. The presence of the C_3AH_{8-12} phase can not be confirmed. Characteristic diffractions of a very low intensity indicate the presence of α-Al_2O_3. The presence of calcite could be indentified.

The specimens fired at 1 100 °C contain larger quantities of CA_2 and CA, besides a small amount of $C_{12}A_7$. The heating up to 1 200 °C did not substantially affect the composition of the specimen, apart from producing a slightly larger quantity of the CA_2 phase. The specimens that have been heated to 1 300 °C did not contain $C_{12}A_7$, but smaller quantities of mullite ($3 Al_2O_3 . 2 SiO_2$) produced by crystallization of the fibres, were observed.

The phase compositions of the individual specimens are shown by the X-ray patterns in Fig. 1. which have been prepared by means of a plotter supplied with the Hewlett Packard 9820 A calculator.
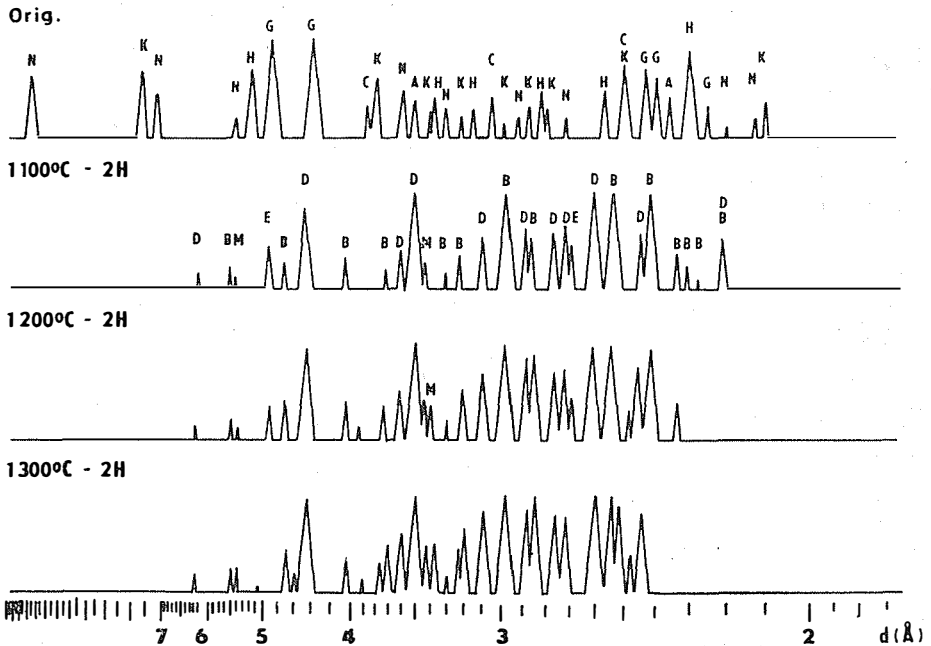

Fig. 1. X-ray patterns of specimens with alumina cement.

A — αAl_2O_3	G — $Al_2O_3 . 3 H_2O$ (*gibbsite*)
B — CA	H — C_3AH_6
C — *calcite*	K — $C_3A . CaCO_3 . 12 H_2O$
D — CA_2	M — *mullite*
E — $C_{12}A_7$	N — CAH_{10}

Specimens with alumina cement and silica flue dust

After hydration of the samples considerable quantities of gibbsite and the CAH_{10} phase were determined. It is interesting to note that also small quantities of calcite and $Ca(OH)_2$ were present.

The specimens heated at 1 100 °C contain various quantities of anorthite (CaO . . Al_2O_3 . 2 SiO_2) and gehlenite (2 CaO . Al_2O_3 . SiO_2), besides a small quantity of the CA_2 phase and cristobalite. Also a slight quantity of mullite was identified. Upon heating at 1 200 °C were formed larger quantities of anorthite and gehlenite, somewhat higher mullite content and reduced quantities of CA_2. Heating at the maximum temperature (1 300 °C) decreased the content of cristobalite and CA_2 (Fig. 2).
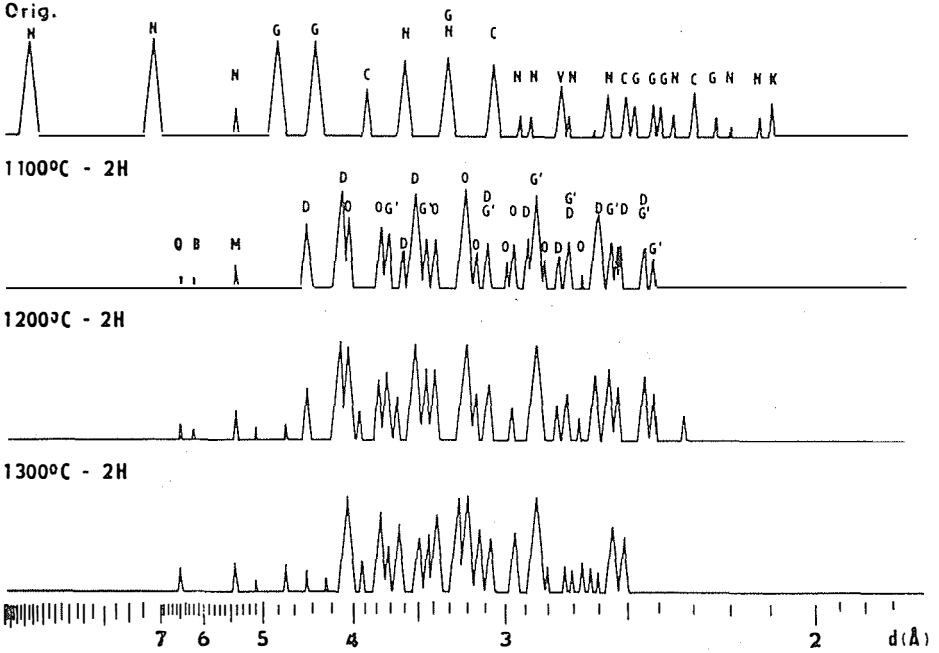

Fig. 2. *X-ray patterns of specimens with alumina cement and silica flue dust.*

B	—	CA	G'	—	gehlenite
C	—	calcite	M	—	mullite
D	—	CA₂	N	—	CAH₁₀
G	—	Al₂O₃ . 3 H₂O	O	—	anorthite
		(gibbsite)	V	—	vaterite

Specimens with Portland cement

Before heat treatment, the specimens were found to contain significant quantities of portlandite ($Ca(OH)_2$), besides low contents of calcite and a certain quantity of non-hydrated clinker minerals (alite, belite and C_3A).

Heating at 800 °C resulted in the formation of secondary belite which was still crystalographically disordered, as indicated by the diffuse character of the respective diffraction peaks. Besides a small amount of calcite was found also a smaller quantity of secondarily produced $Ca(OH)_2$.

100

Upon heating at 1 000 °C β-C$_2$S was formed, the internal structure of which ex-hibited a more ordered character, as indicated by a narrower profile of the diffract-ion peaks. Likewise the initial formation of gehlenite was confirmed. A temperature increase up to 1 100 °C increased significantly the belite contents, whereas the gehlenite quantity remained at the same concentration level. The specimens which were heated at 1 200 °C did not substantially differ from the previous specimen, except for the lower portlandite content. The specimen heated at 1 300 °C differed considerably by its phase composition; its main phase was gehlenite, besides a smaller quantity of pseudowollastonite and belite. Portlandite could no longer be identified (Fig. 3).
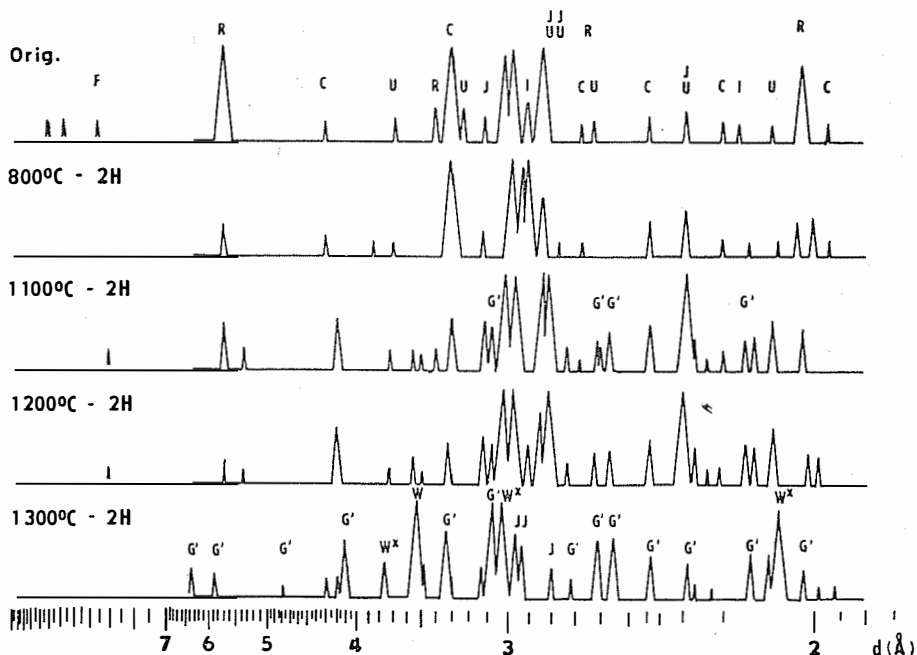

Fig. 3. X-ray patterns of specimens with Portland cement.

C — *calcite*	J — β-C$_2$S
F — C$_4$AF	R — Ca(OH)$_2$
G′ — *gehlenite*	U — C$_3$S
I — C$_3$A	W× — pseudowollastonite

Specimen with Portland cement and silica flue dust

Before heat treatment, the hydrated specimen was characterized by a certain proportion of non-hydrated clinker minerals and a small amount of portlandite, besides a lower quantity of calcite.

Heating at 800 °C yielded a certain quantity of poorly crystallized belite, besides a small quantity of wollastonite. Also smaller quantities of Ca(OH)$_2$ and calcite were identified. Heating at 1 000 °C produced gehlenite and a small quantity of secondary calcite. Firing at 1 100 °C did not change significantly the phase composition, apart from the disappearance of calcite and the identification of small amounts of Ca(OH)$_2$.

At 1 200 °C were identified wollastonite, pseudowollastonite and increased gehlenitȷ contents. Heating at 1 300 °C resulted in the formation of distinct quantities oɘ pseudowollastonite and gehlenite. No further phases could be positively identified in the specimens. The X-ray diffraction patterns for some selected specimens are shown in Fig. 4.
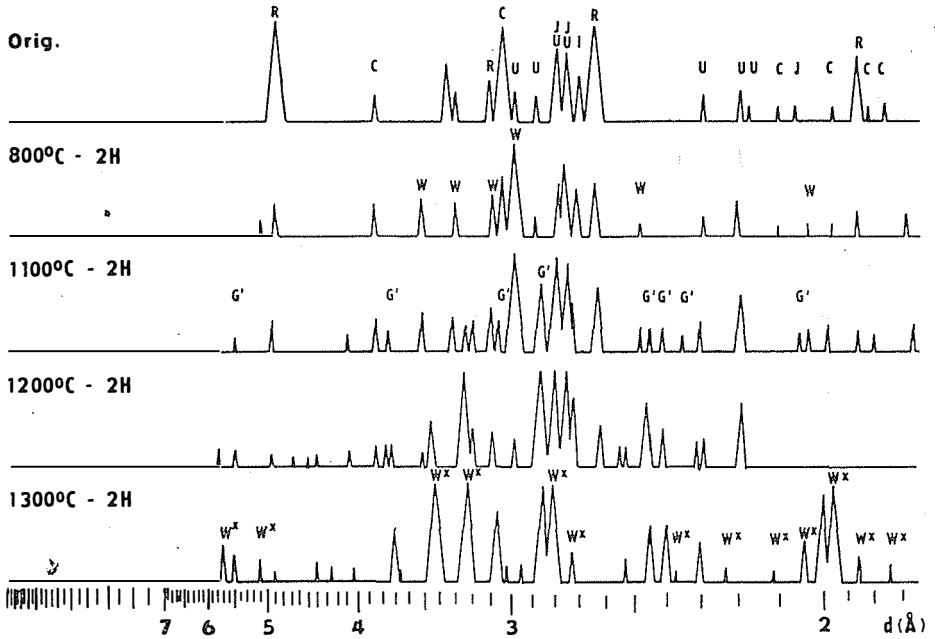

Fig. 4. *X-ray patterns of specimens with Portland cement and silica flue dust.*

C	— calcite	R	— Ca(OH)$_2$
G′	— *gehlenite*	U	— C$_3$S
J	— β-C$_2$S	W	— *wollastonite*
		W×	— *pseudowollastonite*

The microstructure of heat treated specimens

Specimens with alumina cement

The specimen heated at 1 100 °C still contained unchanged ceramic fibres embedded in the cement. The temperature of 1 200 °C changed somewhat the morphology of the dehydrated cement grains that covered the ceramic fibres; as a result of the partial fusion of the fibre surface, the grains were at some points "immersed" in the fibre surface (Fig. 5). Considerable destruction resulting from the melting of the fibres has taken place at the maximum temperature of 1 300 °C (Fig. 6).

The microstructure of the heat treated specimen with additions of silica flue dust exhibited no significant differences from the series with no flue dust additions. The fibres appear virtually unaffected at temperatures up to 1 100 °C and 1 200 °C (Fig. 7). The considerable destruction of the fibres which corresponds by its extent to the specimens without flue dust additions, can readily be seen at 1 300 °C (Fig. 8).

Specimens with portland cement

The formation of isometric grains of the dehydrated cement can be observed at temperatures of 1 000 °C and above (Fig. 9); this was indicated by the formation of a liquid phase. A temperature increase up to 1 100 °C produced a melt which embedded the individual fibres (Fig. 10). A further temperature rise increased the contents of the liquid phase, so that at 1 300 °C no fibre residues could be observed.

Although the formed melt surrounded the fibres in the specimens containing Portland cement and flue dust (Fig. 11), the texture destruction which occurred at 1 200 °C was not as distinct as with the specimen without flue dust contents. The fibres were mutually bound by the solidified melt, and some of the fibres still maintained their original shape (Fig. 12). In the specimens heated at 1 300 °C can be observed only the solidified melt without any residues of the ceramic fibres.

CONCLUSION

The differences in phase composition and microstructure of fibre plate specimens, composed of Resistex R 12 ceramic fibres bonded with Sécar 71 alumina cement or Portland cement with or without the addition of silica flue dust after heating at temperatures up to 1 300 °C were studied. At temperatures from 1 100 °C upwards, a mixture of anorthite, gehlenite and CA_2 is formed in the specimens from alumina cement and silica flue dust. In the absence of flue dust the high-temperature teatment yields the original clinker minerals: CA and CA_2, besides a small amount of $C_{12}A_7$.

After firing at 1 300 °C, the fibres in both series are strongly corroded and embedded in the solidified melt. It was found that the specimens based on Portland cement and silica flue dust contained after heating above 800 °C wollastonite. The formation of gehlenite was determined in both series at temperatures from 1 000 °C upwards.

There are no significant differences in the microstructure of the heat treated specimens of the both series.

But the corrosion of the fibres is considerably less distinct in the series containing the silica flue dust. The specimens were completely molten at a heating temperature of 1 300 °C. The alumina cement is more suitable for this type of application, since it reacts with the kaolin fibres at temperatures which are approx. 100 °C higher in comparison with the materials containing Portland cement.

References

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INTERAKCE MEZI KAOLÍNOVÝM VLÁKNEM A CEMENTEM ZA VYSOKÝCH TEPLOT

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Deskové materiály z hlinitokřemičitých keramických vláken pojených hlinitanovým nebo p-cementem bez přídavku nebo s přísadou vysocekřemičitého úletu amorfní struktury byly tepelně zpracovány do teploty 1300 °C.

Ve vzorcích s Al-cementem a křemičitým úletem vzniká od 1100 °C směs anortitu a gehlenitu vedle fáze CA. Bez úletu byly prokázány pouze původní slínkové minerály: CA, CA$_2$ a malé množství C$_{12}$A$_7$. Vzorky s p-cementem a úletem vykazovaly od teploty 800 °C jistý podíl wollastonitu, od 1000 °C byl zjištěn gehlenit, bez ohledu na přísadu úletu.

Vlákna ve směsi s hlinitanovým nebo p-cementem s křemičitým úletem nepodléhají tak značně korozi ve srovnání s materiály bez přísady. Při teplotě 1300 °C byla vlákna již značně natavená.

Obr. 1. *Schematické rentgenometrické záznamy vzorků s hlinitanovým cementem.*
    A — α-Al$_2$O$_3$ G — Al$_2$O$_3$. 3 H$_2$O (*gibbsit*)
    B — CA   H — C$_3$AH$_6$
    C — *Kalcit*   K — C$_3$A . CaCO$_3$. 12 H$_2$O
    D — CA$_2$ M — *Mullit*
    E — C$_{12}$A$_7$ N — CAH$_{10}$

Obr. 2. *Schematické rentgenometrické záznamy vzorků s hlinitanovým cementem a křemičitým úletem.*
    B — CA   G′ — Gehlenit
    C — *Kalcit*   M — *Mullit*
    D — CA$_2$ N — CAH$_{10}$
    G Al$_2$O$_3$. 3 H$_{20}$ O — *Anortit*
       (*Gibbsit*)   V — *Vaterit*

Obr. 3. *Schematické rentgenometrické záznamy vzorků s p-cementem.*
    C — *Kalcit*   J — β-C$_2$S
    F — C$_4$AF   R — Ca(OH)$_2$
    G′ — Gehlenit   U — C$_3$S
    I — C$_3$A   W× — *Pseudowollastonit*

Obr. 4. *Schematické rentgenometrické záznamy vzorků s p-cementem a křemičitým úletem.*
    C — *Kalcit*   R — Ca(OH)$_2$
    G′ — Gehlenit   U — C$_3$S
    J — β-C$_2$S   W — *Wollastonit*
                                       W× — *Pseudowollastonit*

Obr. 5. *Resistex s Al-cementem (1200 °C).*
Obr. 6. *Resistex s Al-cementem (1300 °C).*
Obr. 7. *Resistex s Al-cementem a křemičitým úletem (1100 °C).*
Obr. 8. *Resistex s Al-cementem a křemičitým úletem (1300 °C).*
Obr. 9. *Resistex s p-cementem (1000 °C).*
Obr. 10. *Resistex s p-cementem (1100 °C).*
Obr. 11. *Resistex s p-cementem a křemičitým úletem (1000 °C).*
Obr. 12. *Resistex s p-cementem a křemičitým úletem (1200 °C).*

ВЗАИМОДЕЙСТВИЕ МЕЖДУ КАОЛИНОВЫМ ВОЛОКНОМ И ЦЕМЕНТОМ ПРИ ВЫСОКИХ ТЕМПЕРАТУРАХ

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Исследованы различия фазового состава и микроструктуры образцов щитовых материалов, изготовленных из керамических волокон РЕСИСТЕКС Р 12, связанных глиноземистым цементом СЕКАР 71 или п-цементом с добавкой или без добавки высокосиликатного уноса — после тепловой обработки до 1300 °C. В образцах с Al-цементом и силикатным уносом возникает от 1100 °C смесь анортита и гелнита помимо CA$_2$. Без уноса возникают первоначальные клинкерные минералы: CA и CA$_2$ наряду с меньшей долей C$_{12}$A$_7$.

После тепловой обработки до 1300 °C волокна обеих серий являются значительно разрушенными и обертываются затвердевшим расплавом. В образцах с п-цементом и силикатным уносом от температуры 800 °C доказано возникновение волластонита и от 1000 °C у обеих серий образование гелнита.

Микроструктура термически обработанных образцов обеих серий взаимно существенно не отличается.

У волокон смеси с силикатным уносом нет такового выразительного разрушения цо сровнению с серией без указанной добавки. При температуре обжига 1300 °C образцы вполне расплавились. Глиноземистый цемент является для этого типа применения более подходящим, так как он реагирует с каолиновым волокном при температуре приблизительно на 100 °C выше по сравнению с п-цементом.

Рис. *1. Схематические рентгенозаписи образцов с глиноземистым цементом.*

A — α—Al_2O_3 G — $Al_2O_3 . 3 H_2O$ (гибсит)
B — CA H — C_3AH_6
C — *Кальцит* K — $C_3A . CaCO_3 . 12 H_2O$
D — CA_2 M — *Муллит*
E — $C_{12}A_7$ N — $CĀH_{10}$

Рис. *2. Схематические ренгтенозаписи образцов с глиноземистым цементом и силикатным уносом.*

B — CA A‘ — *Геленит*
C *Кальцит* M — *Муллит*
D CA_2 N — $CĀH_{10}$
G $Al_2O_3 . 3 H_2O$ O — *Анортит*
 (гибсит) V — *Ватерит*

Рис. *3. Схематические рентгенозаписи образцов с п-цементом.*

C — *Кальцит* J — β—C_2S
T — C_4AF R — $Ca(OH)_2$
G‘ — *Геленит* U — C_3S
I — C_3A W* — *Псевдоволластонит*

Рис. *4. Схематические рентгенозаписи образцов с п-цементом и силикатным уносом.*

C — *Кальцит* R — $Ca(OH)_2$
G‘ — *Геленит* Y — C_3S
J — β—C_2S W — *Волластонит*
 W* — *Псевдоволластонит*

Рис. *5. Ресистекс с Al-цементом (1200 °C).*
Рис. *6. Ресистекс с Al-цементом (1300 °C).*
Рис. *7. Ресистекс с Al-цементом и силикатным уносом (1100 °C).*
Рис. *8. Ресистекс с Al-цементом и силикатным уносом (1300 °C).*
Рис. *.9. Ресистекс с п-цементом (1000 °C).*
Рис. *10. Ресистекс с п-цементом (1100 °C).*
Рис. *11. Ресистекс с п-цементом и силикатным уносом (1000 °C).*
Рис. *12. Ресистекс с п-цементом и силикатным уносом (1200 °C).*

KRYŠTÁLOVÁ ŠTRUKTÚRA PYROFYLITU bola spresnená na základe monokryštálových röntgenografických údajov po R-faktor 0,060 (Lee Jung Hoo, Guggenheim S.: Am. Mineral. *66*, 350 (1981)). Doterajšie vedomosti o štruktúre tohoto polytypického minerálu sa pre nedostatok vhodného materiálu zakladali iba na meraniach neusporiadaných kryštálov alebo polykryštalických preparátov. Monokryštály pyrofylitu vhodné pre röntgenoštruktúrnu analýzu sa našli na nedávno objavenom ložisku neďaleko Ibitiara- Bahia v Brazílii. Ložisko je hydrotermálneho pôvodu a veľkosť kryštálov pyrofylitu dosahuje až 5 cm. Výsledky štruktúrnej analýzy potvrdili polytyp 1TC v súhlase s pôvodným modelom B. B. Zvjagina.
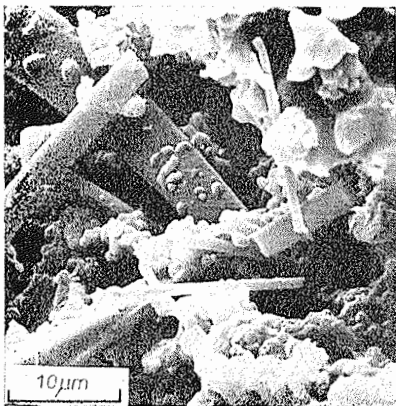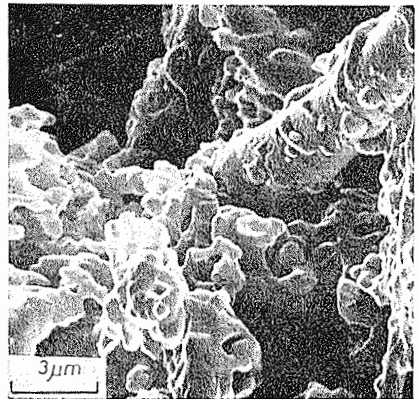
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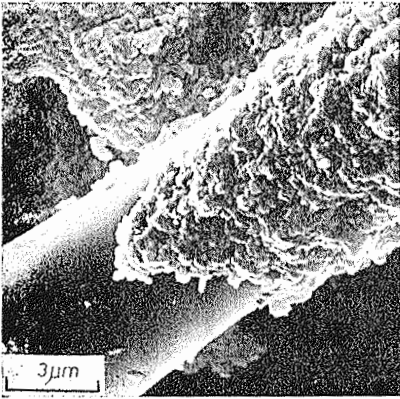
Fig. 5. Resistex with alumina cement
(1200 °C).
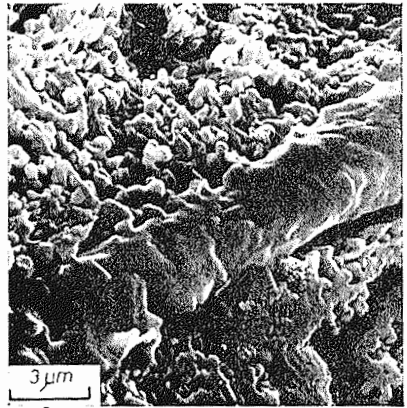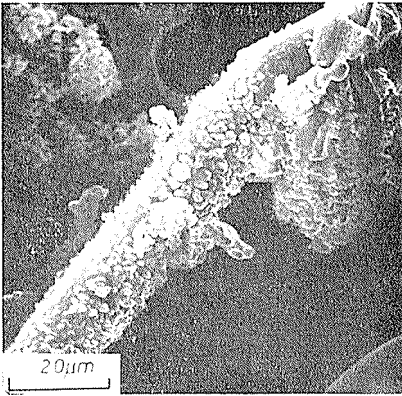

Fig. 6. Resistex with alumina cement
(1300 °C).
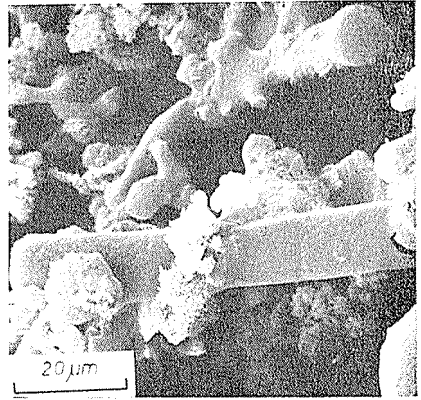

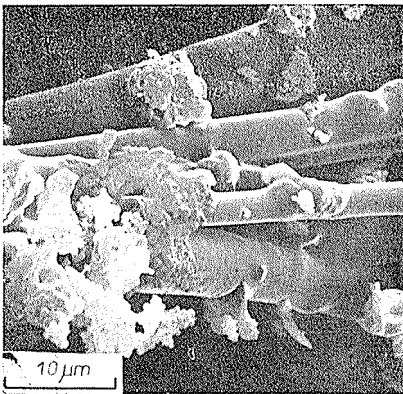Fig. 7. Resistex with alumina cement and
silica flue dust (1100 °C).

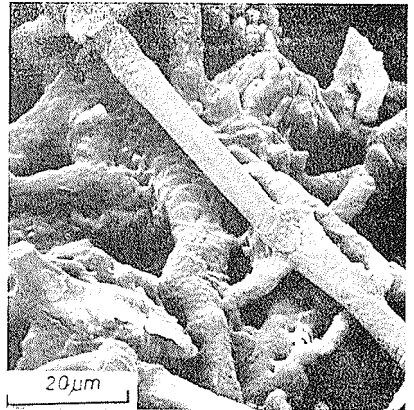Fig. 8. Resistex with alumina cement and
silica flue dust (1300 °C).

Fig. 9. Resistex with Portland cement
(1000 °C).

Fig. 10. Resistex with Portland cement
(1100 °C).

Fig. 11. Resistex with Portland cement and
silica flue dust (1000 °C).

Fig. 12. Resistex with Portland cement and
silica flue dust (1200 °C).