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EVALUATION OF POTASSIUM TITANATE AS A COMPONENT OF ALKALINE FUEL CELL MATRICES

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16. Abstract

Various forms of potassium titanate were found to have almost complete resistance to chemical attack in 45 wt % KOH at 150° C (423 K) for up to 9600 hours. Electron microscopy and X-ray diffraction disclosed important differences with respect to fibricity and stability. The octatitanate appeared to possess the best combination of properties. It was concluded that potassium titanate could be produced in a more asbestos-like form. Fiber dispersion is important in matrix manufacture.

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EVALUATION OF POTASSIUM TITANATE AS A COMPONENT OF ALKALINE FUEL CELL MATRICES

by Robert E. Post

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SUMMARY

This work examined representative forms of potassium titanate for durability in a hot caustic environment, size and shape of particles, and chemical and crystallographic characterization. Possibilities for upgrading the material for use in fuel cell matrices were also explored as well as suitable test methods for screening purposes. Matrix testing in fuel cells was not part of this work. The forms examined were fibrous tetra- and octatitanates, fibrous variations of tetratitanate and acicular and nonacicular hexatitanates. All forms were resistant to 45 weight percent potassium hydroxide at 150° C (423 K) for 500 hours. The fibrous variations of tetratitanate exhibited some fiber degradation at 9600 hours. No samples showed any changes of weight or alkali balance that could be correlated with degradation. The octatitanate appeared to possess the best combination of properties.

A facile exchange of potassium ions for protons was indicated for the tetratitanate and its variations.

During manufacture, the crystals are grown in clusters that are ordinarily exfoliated mechanically with considerable breakage. The fibers are further subdivided into fibrils that undergo separation in caustic environment. Chemical exfoliation from the outset should result in more asbestos-like fibers.

Fractionation of a fibrous form disclosed a wide variety of particle sizes and shapes including much nonfibrous and colloidal material. A tendency to form clusters of fibers was also observed. Filtration of slurries of the samples tended to result in larger clumps of fibers. The clump size is related to the interval between cracks observed in the surface of a commercial matrix. Good dispersion of fibers is required in matrix manufacture.

Scanning and transmission electron microscopy and X-ray diffraction were found useful as measures of actual and potential degradation.

INTRODUCTION

In a fuel cell employing a matrix to serve the functions of electrode separation and electrolyte containment, the matrix may be a limiting factor with respect to the following aspects:

(1) Compatibility with the electrolyte

(2) Ionic conductivity through the matrix

(3) Effectiveness as a barrier to reactant gas crossover, which is related to pore size and bubble pressure

(4) Mechanical properties such as strength and flexibility.

In all respects except the first, asbestos has proved to be well suited for use in alkaline fuel cells. However, asbestos tends to degrade in alkali, and the rate of degradation increases markedly with increases in temperature and alkali concentration (ref. 1).

Fibrous potassium titanate has been substituted for asbestos as a major component of fuel cell matrices with some degree of success (ref. 2). It is much more resistant than asbestos to chemical attack by potassium hydroxide (KOH) solutions (ref. 1), and matrices made from commercial grades of potassium titanate compare favorably with asbestos in their overall ability to absorb and retain electrolyte (ref. 1).

However, potassium titanate matrices are distinctly inferior to asbestos matrices with respect to strength and flexibility (ref. 1). In order to obtain acceptable mechanical properties of matrices made with potassium titanate, it has been blended with asbestos and polytetrafluoroethylene (PTFE) (refs. 1 to 3). Even so, the bubble pressures of potassium titanate composite matrices are generally substantially lower than bubble pressures of asbestos matrices (ref. 1) suggesting larger pore sizes or cracks. Another factor that can affect fuel cell performance is a tendency toward the loss of alkali from the electrolyte when potassium titanate constitutes a major portion of the matrix (ref. 3).

Fibrous and acicular alkali resistant potassium titanates of the general formula $K_2O(TiO_2)_n$ have been available for over 10 years (ref. 4). Potassium tetratitanate ($n = 4$), hexatitanate ($n = 6$), and octatitanate ($n = 8$) have been characterized by X-ray diffraction (refs. 4 to 6). The tetra- and hexatitanates are prepared by crystallization from fused salt or supercritical aqueous solution (refs. 4 and 7). The octatitanate is made by heat treatment of acid-leached tetratitanate (ref. 5). The chemical stability is greatest for the hexatitanate and least for the tetratitanate (refs. 5 and 6). The tetra- and octatitanates are much more fibrous than hexatitanate (ref. 5). The crystals of hexa- and tetratitanate are grown in clusters which are commercially exfoliated in a colloid mill. This mechanical exfoliation drastically reduces the length of the fibers which may easily be several millimeters long originally (ref. 4).

The most widely used asbestos substitute has been pigmentary potassium titanate (PKT), which has values of n that very from lot to lot (refs. 1 and 2), sometimes ex-

ceeding eight, and X-ray diffraction patterns that do not consistently show a close correspondence with tetra-, hexa-, or octatitanates (ref. 2).

The crystal structure of the alkali metal titanates has been studied by Anderson and Wadsley (ref. 8) and by Wadsley and Mumme (ref. 9). These workers concluded that the alkali metal titanates are tunnel structures with the tunnels running parallel to the fiber axis and with variations in the degree of order and in lateral access.

The purpose of this work was to relate the nature of the material to its performance in matrices. The work began as a classification of existing materials with respect to their suitability in matrix manufacture. The study of basic characteristics led to conclusions concerning avenues of improvement with respect to the best starting material and treatments that would optimize desirable characteristics. This work also embraced the study of test methods used in the evaluation of materials for their suitability as matrix components.

The materials examined were some representative samples provided by the only known manufacturer.[1] These included tetra-, hexa-, and octatitanates, a PKT and some modified materials. The effects on stoichiometry of drying, exposure to 45 weight percent KOH solution at 150° C (423 K), and various leaching processes were determined. Treated material was examined for structural changes using electron microscopy and X-ray diffraction. The nature of individual particles, agglomerates, and matrix surfaces was also examined by electron microscopy.

From the information thus obtained, inferences were drawn with respect to the relation of fiber morphology, stoichiometry, and crystal structure to performance of potassium titanate matrices in fuel cells.

The manufacture and testing of matrices in working fuel cells were not a part of this work.

DESCRIPTION OF SAMPLES

Sample A. - A fibrous material having characteristics similar to pigmentary potassium titanate (PKT), apparently a variation of tetratitanate

Sample B. - Fibrous tetratitanate, acid leached to pH 5

Sample C. - Fibrous tetratitanate

Sample E. - Acicular (elongated crystals, but not notably fibrous) hexatitanate

Sample F. - Fibrous octatitanate, formed from tetratitanate by acid leaching and calcining

Sample G. - Nonacicular hexatitanate

Sample H. - Barium stabilized acicular hexatitanate

[1] E. I. duPont de Nemours and Co., Wilmington, Del.

EXPERIMENTAL DETAILS

Treatments

The equipment for the caustic exposure tests consisted of a polytetrafluoroethylene (PTFE) capsule, to contain the mixture without contamination, inside a metal capsule that sealed against loss of water vapor.

A determination was made of the amount of water driven off from all samples at 150° C (423 K), partly as a determination of the hygroscopicity of the as-received materials, and, perhaps of more practical significance, in order to afford a common basis with respect to the material that would be obtained later after the hot caustic soak.

Another preliminary consideration was the intention to simulate the proportions of liquid and solid that would exist in a fuel cell. An initial test on type A showed that a firm paste was obtained with 22 grams of 45 weight percent KOH solution per 3 grams solid. All samples were started with this proportion, but the hexatitanate types (samples E, G, and H) formed slurries. When the pressure seals failed on the capsules containing G and H, they were restarted with paste-forming proportions of 11.6 grams solution to 3 grams solid for G and 14.5 grams solution to 3 grams solid for H.

The KOH solution was added to a weighed amount of solid under vacuum to promote penetration. After exposure (500 or 9600 hr) at 150° C (423 K), the material was washed from the capsule, slurried in about 300 cubic centimeters of water and filtered in a centrifugal filter. The filter cake was washed in more water to bring the filtrate volume to nearly 1000 cubic centimeters, and finally the total volume was made up to 1000 cubic centimeters in a volumetric flask. Distilled water was used throughout. Aliquots of the solution were tetrated for total alkali. The filter cake was dried overnight at 150° C (423 K) and weighed (with allowance for the effect of exposure to the above conditions on the weight of the filter paper) to determine change in weight of the solid. The weight change was based on the dried weight of the original material. To get a little more information on the nature of the water content, one sample of PKT (sample A) was heated at 300° C (573 K) to determine if any additional water would be driven off.

Fractionation by sedimentation was carried out by the simple process of repeated slurrying and decanting. In another experiment a slurry was allowed to settle while the water evaporated in a forced circulation oven.

The leaching procedure was a series of slurrying steps and filtrations. Each slurry contained 3 grams of solid in water or a solution of sodium chloride of sufficient concentration to coagulate colloidal material. The pH of the slurries was measured to indicate the extent of ion exchange.

Titration was performed potentiometrically on slurries with 0.1 normal hydrochloric acid to an apparent end point at about pH 3.

ANALYTICAL METHODS

The following analytical methods were employed.

(1) X-ray diffraction to determine the crystalline form of the potassium titanate and to observe any changes brought about by treatment

(2) Electron microscopy, scanning and transmission, to determine the kinds of fibers and other particles present and also to observe the structure of agglomerated material

(3) Chemical analysis of solids to determine the stoichiometry of the materials

(4) Material balance on treated samples to determine changes in weight and potassium content

Experimental error was estimated for material balances on the basis of the limitations in the analytical methods. For direct titrations, even with small amounts delivered from the buret, relative errors of about 1 percent would be maximum and the results generally significant. In the case of material balances on the treated samples, a small-difference-of-large-numbers effect causes a considerable increase in error. The magnitude is given with the data in table I. The estimate of error in the chemical analysis of solids is based on replicate determinations.

RESULTS

Comments on Organization of Data

The conclusions from this work require the correlation of the results from the various tests. For purposes of comparison the results have been condensed into three tables. The stoichiometric data from the hot caustic exposure tests are given in table I. The comparative results of all methods of examination, including qualitative inferences from the stoichiometry, are given in table II. The fractionation and leaching tests were performed on type A only. The information obtained from these experiments is presented in table III. These last experiments were conducted mainly to reveal the nature of a typical pigmentary material with respect to mechanical aspects of matrix manufacture and behavior. Therefore, some other pertinent observations on material and matrix properties are also placed in table III.

Results from microscopy are illustrated by photographs selected to show as many effects in as few pictures as possible. Therefore, descriptions of a given sample may refer to a picture of another material.

General Comments

The most accurate data are for the change in weight of solids. There were both increases and decreases but no indication that any samples were materially degraded by hot caustic exposure.

The experimental error is relatively large for the material balance by chemical analysis of solids and by determination of total alkali difference. However, there seem to be some correlations with other observations, and these are set out in table II.

Some of the error in total alkali difference arises from the strong tendency for at least some kinds of potassium titanate to exchange ions. This is shown by the entries for types A and B at 9600 hours of exposure before and after reslurrying the filtered solids with water. The difference, which, being the direct titration of the filtrate, has less than 1 percent error, is as large as the estimated error of analysis.

Some of the error in chemical analysis of solids is probably sampling error, including stratification of solids during filtration. This factor could also be important in examination by X-ray diffraction and microscopy.

No trace of titanium could be found in the caustic solutions. This fact was used in the material balance calculations from chemical analysis of solids where invariance of titanium content was assumed.

The material balance for potassium as determined by either total alkali difference or by chemical analysis of solids is shown in terms of potassium-hydrogen exchange $\Delta(K\text{-}H)$. The choice of this quantity is based on the agreement between it and the measured weight change for the titrated specimens of original samples A and B, where the experimental error is at a minimum.

The octitanate (type F) was not available at the outset of this work and was not tested for 9600 hours.

DISCUSSION

Background

The background for interpretation of the behavior of potassium titanates can be set by consideration of the crystal structure deduced by Andersson and Wadsley (ref. 8) and by Wadsley and Mumme (ref. 9). The structures (fig. 14) are characterized by ribbons of titanium-oxygen octahedra. The ribbons enclose tunnels parallel to the fiber axis. Alkali metal ion sites are located in the tunnels. All sites are filled in the hexatitanate, but not in some of the other types. Lateral apertures are also found (fig. 14(b) and (d)), the nature of which varies with the type of titanate. The crystalline order is greatest for the hexatitanate and least for the tetratitanate. The disorder is essentially in the

lateral direction. It is not clear whether the alkali metal ions should be mobile; however, the literature (refs. 4 to 6 and 10) indicates that ion exchange takes place more or less readily, with the most stable form, the hexatitanate, being the most resistant. There is also a parallel between fibricity, disorder, and exchange of ions and water. The search for an optimum with respect to low potassium content, a high degree of fibricity, and minimum hygroscopicity led to the development of the octatitanate (ref. 5). An important step of the process involves ion exchange in the disordered tetratitanate. Figure 14 indicates that lateral access in the tetratitanate should be readily available, whereas for the octatitanate and hexatitanate it should be rather restricted.

Material Balance

As it turned out there was no evidence of degradation obtained from material balance data, and the only significant result from material balance determinations was some data on the tendencies of the materials to exchange ions and water (tables I and II). For the initial drying at 150° C and the 500-hour hot caustic treatment, the most regularly crystalline materials were affected the least, with hygroscopicity increasing in the order hexa-(E), octa-(F), tetratitanate (C). With respect to the effects of the 500-hour caustic treatment and processing of the samples, none of these three types seemed to be significantly changed. However, acid-leached tetratitanate (B) gained potassium, as would be expected, and the PKT(A) also gained potassium, suggesting that the initial value of $n = 6.8$ corresponded not to hexatitanate but to a possible poorly developed tetratitanate that was leached in processing. The PKT(A) had about the same amount of free water (i.e., water driven off at 150° C (423 K)) as the tetratitanate, while the acid-leached tetratitanate (B) was typically high in this respect (ref. 5).

The nonfibrous materials are of little interest as principal constituents of fibrous matrices, but it is of some interest that considerable barium was extracted from sample H, indicating that this modification is probably not useful for fuel cell applications.

The tetratitanate (C), acid leached tetratitanate (B), and PKT(A) were given the hot caustic treatment for 9600 hours. Only the tetratitanate seemed to be affected more than it had been from the 500-hour treatment, with a small loss of potassium indicated.

X-ray Diffraction

The X-ray diffraction (XRD) information (table II) shows some relation to the stoichiometry. The hexatitanate and octatitanate (samples E and F) were unchanged by exposure to hot caustic for 500 hours. For tetratitanate and acid leached tetratitanate

(samples C and B), phase transitions to more stable forms are evident with the acid leached tetratitanate going over to mostly octatitanate while the tetratitanate shows a small increase in both hexa- and octatitanates. The PKT sample underwent no permanent change that could be associated with caustic treatment; rather the effects were mostly those that would be associated with lattice distortions, such as broadening and shifting of the diffraction peaks.

The distortion of X-ray diffraction patterns was a typical result of stoichiometric imbalance. Broadening or shifting of peaks was associated with residual alkali (compare A500 with A9600 reslurried), with acid titration, observed in sample A, B, and C, and with moisture absorption (note the poor patterns obtained with leached and fractionated material (table III)). Considerable shifting occurred in titrated PKT(A). This sample had been allowed to soak at a pH of about 3 for 3 days. The resulting pattern did not correspond with any reference species, suggesting extensive changes in the lattice. Less drastic treatment appeared to be reversible to some extent. In particular, moisture absorption in PKT(A) would destroy the patterns almost completely, but sharpness would return on drying.

The presence of water in the lattice itself is indicated by two observations. First, the water driven off at 300° C (573 K) is 2.6 percent greater than at 150° C (423 K). Second, the correspondence of weight change and alkali balance for titrated samples, where error is relatively small, is obtained by assuming an exchange of potassium ions with protons or of hydrated potassium ions with hydronium ions.

Electron Microscopy

The fibrous materials had much the same overall appearance at a magnification of 1000 (fig. 1). The finest fibers were observed in the sample of PKT(A), but there seemed to be more fibers over 20 micrometers long in the octatitanate sample (F). The acicular hexatitanate (E) particles are relatively long but also relatively thick (fig. 6). The lesser ability of hexatitanate forms (samples E, G, and H) to absorb electrolyte is no doubt related to particle thickness.

At 500 hours the hot caustic soaked samples showed no apparent degradation at a magnification of 1000. After 9600 hours the PKT(A) and acid leached tetratitanate (B) showed some fiber shortening and the presence of stubby material (fig. 2). The tetratitanate (C) did not seem to be much degraded.

At a magnification of 125 000 some physical changes are evident. In the fibrous types there is a separation of fibers into fibrils, which, being a finer subdivision, make the material more like asbestos. However, some of the fibrils appear to be broken into colloidal fragments (fig. 3). The tetratitanate (C) seemed best able to withstand the breakage (fig. 5). Except for the acid leached tetratitanate (B), the fibrous materials

had bristles on the fiber ends (fig. 3). Acicular hexatitanate (E) had stubs (fig. 7). Acid leached tetratitanate (B), which converted into octatitanate, had a greater fibril thickness compared with the tetratitanate (sample C) from which it was made (fig. 4). These observations, together with the absence of a detectable amount of soluble titanium in alkaline solutions, suggest that recrystallization occurs. The material for crystal growth must come from disordered interfibril regions, from surfaces, or from colloidal particles. Except for the acid leached tetratitanate, crystal growth seems to be preferred as an extension of a substructure in the longitudinal direction. In the case of acid leached tetratitanate, the growth seems to be in a lateral direction and is apparently associated with the phase change to octatitanate.

The amount of bristle growth and fibrillation did not seem to be proportional to the duration of exposure. This could mean that the readily soluble material was rapidly consumed. On the other hand, it could be attributable to the fact that the material was in the form of a heavy paste which limited mass transport.

Leaching and Fractionation

A greater and much more rapid degradation than that observed in alkali occurred as a result of prolonged leaching with water and salt solution (fig. 8). Caustic seems to have a protective effect.

Fractionation of PKT(A) disclosed an appreciable amount of relatively long and fine fibered material (figs. 9 and 10). However, there were also disconcerting amounts of chips, short fibers, and colloidal material, some of which seemed to bind clusters (fig. 10). All types of potassium titanate observed seemed to contain some colloidal material.

Fibrous potassium titanate has a pronounced tendency to form clumps with dimensions of the order of 100 micrometers (fig. 11). This dimension is also characteristic of the space between cracks in a matrix surface (fig. 12).

On a somewhat smaller scale, clusters of alined fibers with similar lengths form, particularly when fractionation is attempted in distilled water (fig. 9).

An overall comparison of PKT and asbestos in matrices can be seen by comparing figures 12 and 13. Superficially, the asbestos matrix seems to have a more open structure than the PKT matrix. However, there is actually an abundance of very fine fibers among some very coarse ones.

CONCLUSIONS

The potassium titanate available for use in fuel cell matrices has not been opti-

mized for that purpose. In particular, the pigmentary form (PKT), which was a mainstay for several years, is somewhat susceptible to chemical degradation, though still far superior to asbestos in this respect. Basically, the nature of the fibers in all forms is unsuitable for matrices with good mechanical properties. The utility of PKT is further impaired by the presence of nonfibrous and colloidal matter.

The octatitanate is probably the most suitable form known commercially. (However, at this writing no potassium titanate is being produced.) It is fibrous and quite resistant to ion exchange and water absorption. This resistance to mass exchange should minimize disruption by osmotic forces. If the tetratitanate starting material for the production of octatitanate is carefully made, the octatitanate can be expected to have an inherently stable structure with respect to both lateral and longitudinal attack.

To obtain fine fibers in greater length than the commercial material, it will evidently be necessary to avoid mechanical exfoliation of the crystal clusters. The caustic-induced fibrillation of all the materials based on tetratitanate suggests that chemical exfoliation may be feasible. Fine, splayed fibers with lengths in the millimeters would indeed be more asbestos-like.

In the engineering of matrices with available or improved materials, considerable attention must be given to dispersion of the fibers since they tend to cluster and clump. Nonfibrous material and material that does not comprise fibers at least 10 micrometers long and less than 1 micrometer thick can probably be removed to advantage. It is possible that a controlled amount of short material may be useful in matrix manufacture as a filler of small voids. However, particles small enough to be washed out should be eliminated, because if a fuel cell is refurbished by flushing with water and replacing the electrolyte with fresh solution, some of the colloidal material could be carried into the electrodes where it would be expected to reduce the hydrophobic character of wet-proofed electrodes.

Potassium titanate fibers are naturally cohesive, which can contribute to the formation of brittle matrices. The use of incompatible additives such as PTFE may serve to confer flexibility, but other substances may work just as well. And conceivably a material that serves this function during fabrication and that can then be washed out may be equally satisfactory without introducing an element of hydrophobicity.

Evaluation of material should begin with a fractionation procedure because of the existence of a wide variety of shapes and sizes, which may be associated with variations of stoichiometry and crystal structure. The scanning electron microscope is recommended for resolving shapes and sizes. The transmission electron microscope is recommended for observations of fiber-fibril conformation. X-ray diffraction is perhaps most useful as a measure of homogeneity and stability of the crystal structure.

If there exists an accelerated test for the stability of potassium titanate, it is probably simply repeated slurrying in water.

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Cleveland, Ohio, June
506-23.

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TABLE I. - EFFECT OF EXPOSURE TO 45 WEIGHT PERCENT KOH SOLUTION AT 150° C (423 K) ON VARIOUS FORMS OF POTASSIUM TITANATE AND COMPLEMENTARY ANALYTICAL DATA

[KOH solution concentration, 45 wt %; exposure temperature, 150° C (423 K).]

Sample	Type	Hours of exposure	Other treatment	Chemical analysis of solids					Material balance by total alkali and weight	
				K wt %	Ti wt %	n	$K_2O + TiO_2$ wt %	Fraction weight change as (K-H)	Fraction weight change as (K-H)	Fraction weight change gravimetric
			(a)			(b)		(c)	(c)	(d)
				Maximum error estimate						
				2%	2%	4%	±2	±0.02	±0.02	±0.005
Fibrous pigmentary	A	0	As received	11.48	47.85	6.8	94	-----	------	------
		0	Dried at 423 K	-----	-----	----	--	-----	------	-0.016
		0	Dried at 573 K	-----	-----	----	--	-----	------	-.042
		500	----------	14.58	46.72	5.2	96	0.03	0.03	.046
		9600	----------	-----	-----	----	--	-----	.03	.031
		9600	Reslurried	12.38	46.78	6.2	93	.01	0	------
		9600	Reslurried, titrated	5.30	50.65	15.6	91	-0.06	-.06	------
		0	Titrated	4.06	52.28	21.0	92	-.08	-.074	-.074
Fibrous tetra, acid leached	B	0	As received	7.35	51.29	11.4	94	-----	------	------
		0	Dried at 423 K	-----	-----	----	--	-----	------	-0.025
		500	----------	12.98	47.98	6.0	96	0.06	0.06	.061
		9600	----------	-----	-----	----	--	-----	.06	.079
		9600	Reslurried	12.75	48.28	6.2	96	.06	.03	------
		9600	Reslurried, titrated	6.75	51.22	12.4	94	0	-.03	------
		0	Titrated	4.92	52.68	17.5	94	-.03	-.025	-.026
Fibrous tetra	C	0	As received	16.25	45.8	4.6	96	-----	------	------
		0	Dried at 423 K	-----	-----	----	--	-----	------	-0.013
		500	----------	15.45	46.75	4.9	97	-0.01	-0.01	.010
		9600	----------	-----	-----	----	--	-----	-.03	-.012
		9600	Reslurried, titrated	3.13	53.53	27.9	93	-.13	-.15	------
		0	Titrated	-----	-----	----	--	-----	-.160	------
Fibrous octa	F	0	As received	9.30	50.58	8.9	96	-----	------	------
		0	Dried at 423 K	-----	-----	----	--	-----	------	-0.006
		500		10.38	49.90	7.9	96	0.01	0	.005
Acicular hexa	E	0	As received	13.25	48.35	6.0	97	-----	------	------
		0	Dried at 423 K	-----	-----	----	--	-----	------	-0.001
		500	----------	12.70	47.94	6.2	95	0	-0.01	-.006
Nonacicular hexa	G	0	As received	12.95	49.05	6.2	97	-----	------	------
		0	Dried at 423 K	-----	-----	----	--	-----	------	-0.002
		500	----------	11.08	49.95	7.4	97	-0.02	-0.02	0
Acicular hexa with Ba	H	0	As received	10.2, (6.1Ba)	45.75	7.3	89	-----	------	------
		0	Dried at 423 K	-----	-----	----	--	-----	------	-0.011
		500	----------	10.8	49.90	7.5	96	0	0	.009

[a] Description of treatments. Dried: overnight in forced circulation oven. Reslurried: in distilled water. Titrated: to about pH 3 as a slurry.

[b] In formula $K_2O \cdot (TiO_2)_n$.

[c] Material balances were calculated from chemical analysis of solids or from total alkali determinations in terms of postulated potassium-hydrogen exchange (K-H). Note agreement between total alkali and gravimetric values for A and B titrated where error is less than 1 percent.

[d] Based on dried weight of filtered solids and original material except for treatment entry labelled "dried" which compares dried and undried original material.

TABLE II. - OBSERVATIONS FROM STOICHIOMETRY, MICROSCOPY, AND X-RAY DIFFRACTION ON THE EFFECT OF EXPOSURE OF VARIOUS KINDS OF POTASSIUM TITANATE TO 45 WEIGHT PERCENT KOH SOLUTION AT 150° (423 K)

Type	Treatment	Stoichiometry (a)	Microscopy (b)	X-ray diffraction (c)
A	As received	1.6% free water	Fibers generally less than 1 μm thick and 8 to 15 μm long	Lines for every reference spacing of tetra-, hexa-, and octatitanate
		4.2% bound water	Many <1/2 μm thick, some up to 2 μm thick; some as long as 30 μm (fig. 1)	
	500 hr	Significant gain in alkali and total weight	No apparent effect at ×1000	Line broadening and shifting
	9600 hr, reslurried	Gain in alkali and weight. Reduced to zero gain in alkali by reslurring in water	Fiber shortening; adherent stubby particles (fig. 2); bristles on ends of fibers; separation of fibers into fibrils; colloidal fragments (fig. 3)	Original pattern; note this was reslurried material
	9600 hr, reslurried titrated	Signficant loss of alkali and increase of n	Like untitrated material without adherent stubby fibers	Loss of resolution
	Original titrated (in acid 3 days)	Large loss of alkali	No apparent effect	Peaks resolvable but no correspondence with reference species
B	As received	2.5% free water	Fibers seem shorter and at least as thick as type A; longest fibers are about 20 μm	Lines displaced but tetra-, hexa-, and octa all appear to be present
	500 hr	Somewhat larger gain in alkali and weight than type A; marked decrease in n	No apparent effect at ×1000; fibril separation, but no bristles on fiber ends; fibrils seem thicker than type C (unleached tetratitanate); colloidal fragments (fig. 4)	Pattern ordered by treatment. Mostly octatitanate with a few tetra- and hexatitanate lines
	9600 hr reslurried	Gain in alkali and weight; gain in alkali not reduced to zero by reslurrying	Fiber shortening seen at ×1000; fibril separation, no bristles; extent of fibril separation not proportional to time of exposure	Similar to 500-hr treated material with somewhat stronger indication of tetratitanate
	9600 hr, reslurried titrated	Net loss of alkali; n back near original value	About the same as untitrated material	More like 500-hr treated material than like 9600-hr treated material
	Original titrated	Large loss of alkali but less than for type A	No apparent effect	Many features in common with titrated 9600-hr treated material
C	As received	1.3% free water	Similar to type B	Good agreement between sample pattern and tetratitanate standard; some hints of hexa- and octatitanate
	500 hr	Indication of small loss of alkali but gain in weight	No apparent effect at ×1000; considerable fibril separation with bristles on fiber ends; seemingly less colloidal fragmentation than for A and B (fig. 5)	Line displacements and stronger hints of hexatitanate
	9600	Loss of alkali	----------	----------
	9600 hr, reslurried titrated	Considerable loss of alkali and increase of n	Fiber shortening not marked ×1000; extent of bristle growth not proportional to time of exposure	Appearance of lines corresponding to tetra-, hexa-, and octatitanate with some shifting
	Original titrated	About same loss of alkali as for 9600-hr treated material		
F	As received	0.6% free water	Most fibers over 10 μm long with many 20 to 30 μm; fibers seem a little thicker than type A	Good correspondence with standard (octa); no other species indicated
	500 hr	Barely signficant increase in weight; no significant change in alkali	No apparent degradation at ×1000; bristles and fibril separation; colloidal fragments	Pattern unchanged
E	As received	0.1% free water	Considerable amount of material thicker than 1 μm; some acicular lengths as long as 30 μm, many 20 μm (fig. 6)	Almost perfect agreement with standard (hexa)
	500 hr	Barely significant loss in weight; no significant change in alkali	Fiber ends show stubes rather than bristles; no fibril separation (fig. 7)	Pattern unchanged
G	As received	0.2% free water	Small chips and fines	Excellent correspondence with standard (hexa)
	500 hr	Slight loss in alkali and increase in n; no weight change	Some flocs appear with the chips and fines	Line locations unchanged; apparent orientation effect
H	As received	1.1% free water	Same as type E	General correspondence with hexatitanate standard but with some shifting of several lines
	500 hr	Slight increase in weight; no significant change in alkali; apparent loss of barium	Same behavior as type E	About the same as original material

[a] Taken from table I where details may be found. A "significant effect" is one where the change is greater than experimental error.

[b] Microscopy column contains information from scanning electron microscopy at ×1000 and from transmission electron microscopy at ×100 000. The descriptions are illustrated by photographs selected to show as many effects in as few pictures as possible. Therefore descriptions of the effect on a given sample may refer to a picture of another material.

[c] X-ray diffraction observations were made by inspection of diffractometer charts. A master chart marked with the angles corresponding to the reference spacings was alined with the chart for the sample. For well-ordered materials the alinement process was direct and simple. When line shifts and loss of resolution occurred it was taken as indicative of disorder.

TABLE III. - EFFECTS OF LEACHING AND FRACTIONATION OF PIGMENTARY POTASSIUM TITANATE AND RELATION TO MATRIX ENGINEERING

Treatment	Stoichiometry	Microscopy (a)	X-ray Diffraction (b)
Leaching with water, NaCl solution, water	n goes from 6.8 to 14.6; alkali loss fraction, as (K-H), = 0.07; pH changes: water 10.8 to 9.5, solution 8.8 to 8.1, water 10.0 to 9.5; solid contains Na	Assortment of undegraded thick pieces, clumped short fibers, and a few fibers like original; fig. 8	Generally weak patterns with peaks corresponding to tetra-, hexa-, or octatitanate; no indication of NaCl or KCl
Fractionated by sedimentation	n goes from 6.8 to 9.6; alkali loss fraction, as (K-H), 0.04; at least 2% free water.	Clusters of fibers of similar length; one fraction predominantly longer than 20 μm and finer than 1 μm; heavier fraction contaminated with chunks; lighter fractions contaminated with fines; fig. 9	General correspondence of peak locations with original material (type A); exposure to atmosphere for a few days results in very poor pattern; reversed by drying; immediate effect of wetting with liquid is much less than from atmospheric moisture absorption
Slurry settled during evaporation	----------	Cohesive glazed surface composed of colloidal material; underside has chips, matted fibers, and bundles; colloidal material seems to cement fibers together at ends of some bundles; fig. 10	----------
Material settled with minimal segregation on centrifugal filter	----------	Clumping observed at ×100 (fig. 11) also at ×1000 (fig. 2)	----------
Material made into a practical composite matrix with asbestos and PTFE	----------	Apparently fine-pored as a whole but cracked; connective effect of asbestos is clear; function of PTFE is not apparent; fig. 12	----------
Asbestos matrix surface for comparison	----------	Superficially, asbestos matrix seems to have more open structure than potassium titanate matrix; however, there is actually an abundance of very fine fibers among some very coarse ones; fig. 13	----------

[a]Contains information from scanning electron microscopy at ×100, ×1000, and ×10 000, and from transmission electron microscopy at ×100 000. The descriptions are illustrated by photographs selected to show as many effects in as few pictures as possible. Therefore, descriptions of the effect on a given sample may refer to a picture of another material.

[b]Observations made by inspection of diffractometer charts. A master chart marked with the angles corresponding to the reference spacings was alined with the chart for the sample. For well-ordered materials the alinement process was direct and simple. When line shifts and loss of resolution occurred it was taken as indicative of disorder.

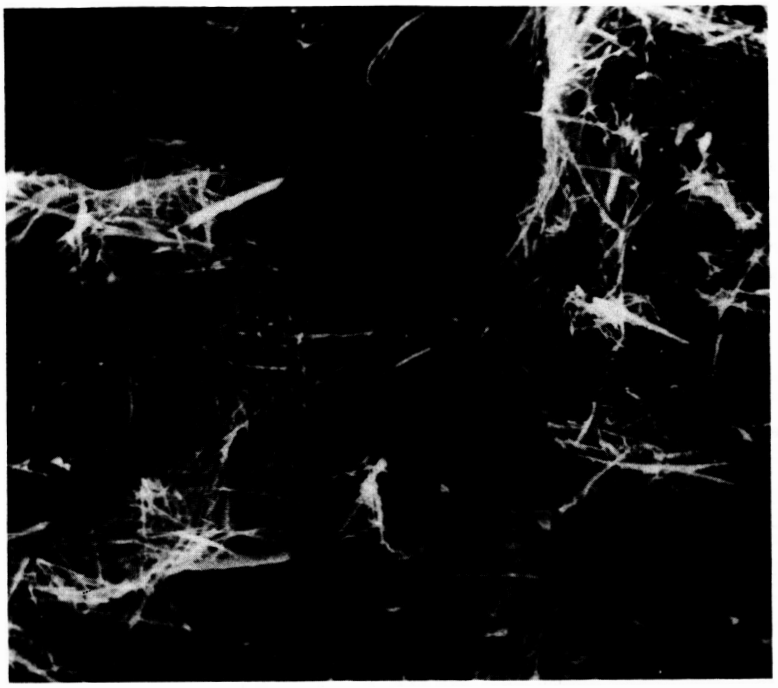


Figure 1. - Character of fibrous materials. X1000.

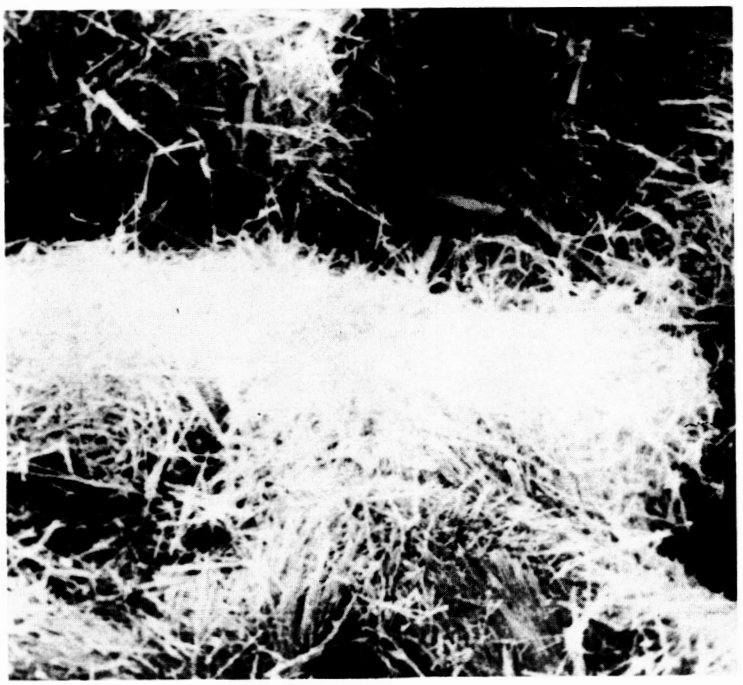


Figure 2. - Fiber shortening after 9600 hours of exposure to hot caustic and clumps. X1000.

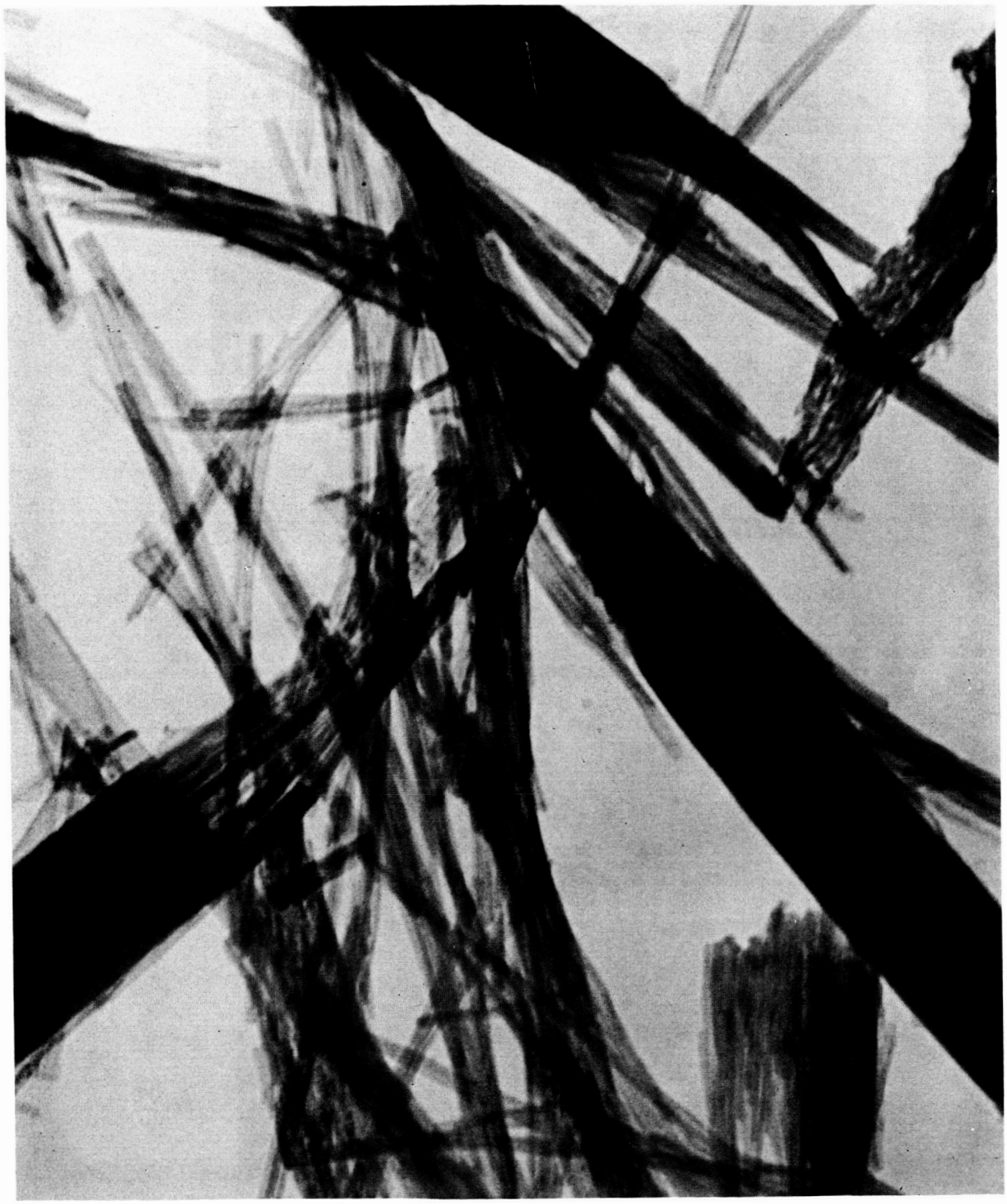


Figure 3. - Bristles, fibril separation, and colloidal fragments. X100 000.

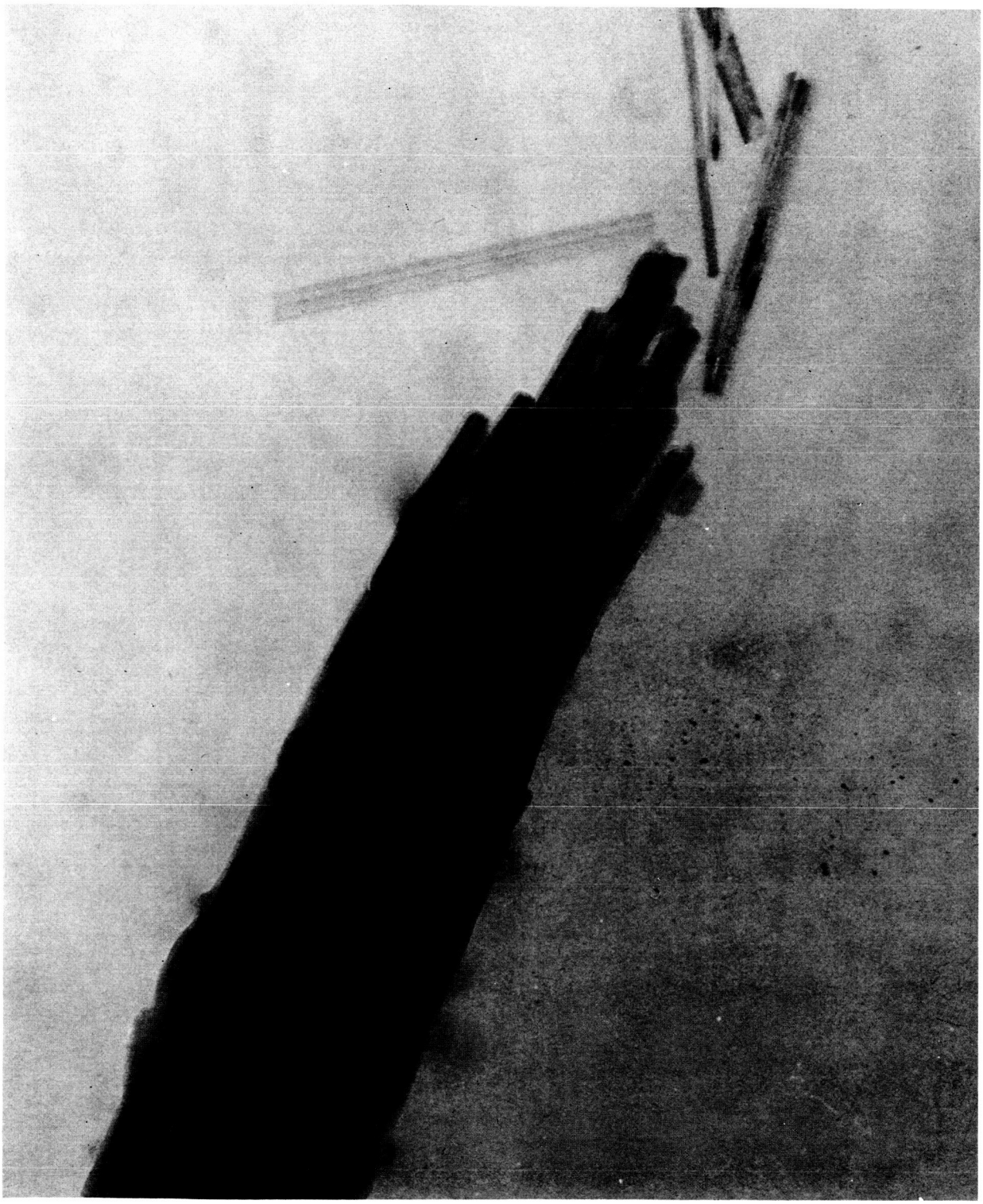


Figure 4. - Lateral recrystallization with fibril thickening of acid leached tetratitanate. X100 000.

Figure 5. - Apparently more stable fibrils of tetratitanate. X100 000.

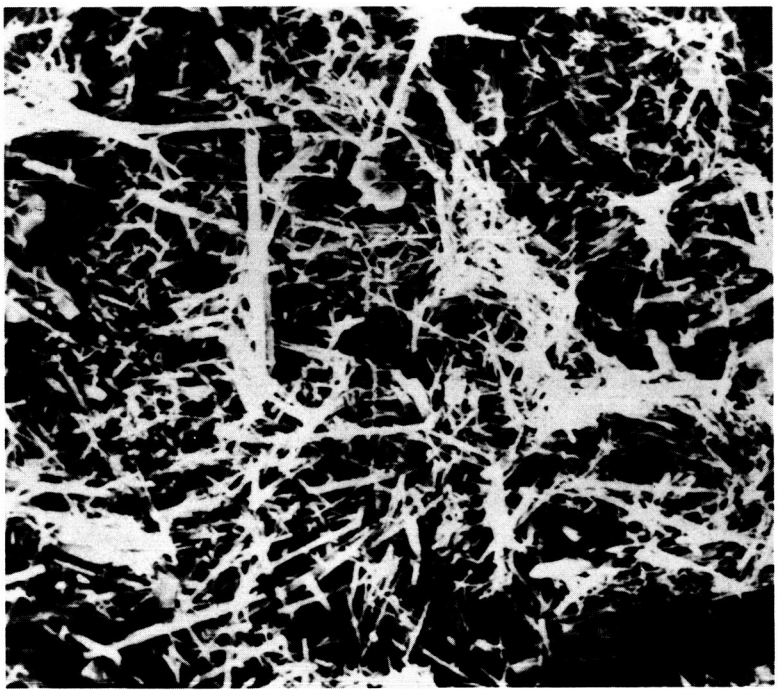


Figure 6. - Acicular hexatitanate. X1000.

Figure 7. - Stub growth on acicular hexatitanate exposed to hot caustic. X100 000.

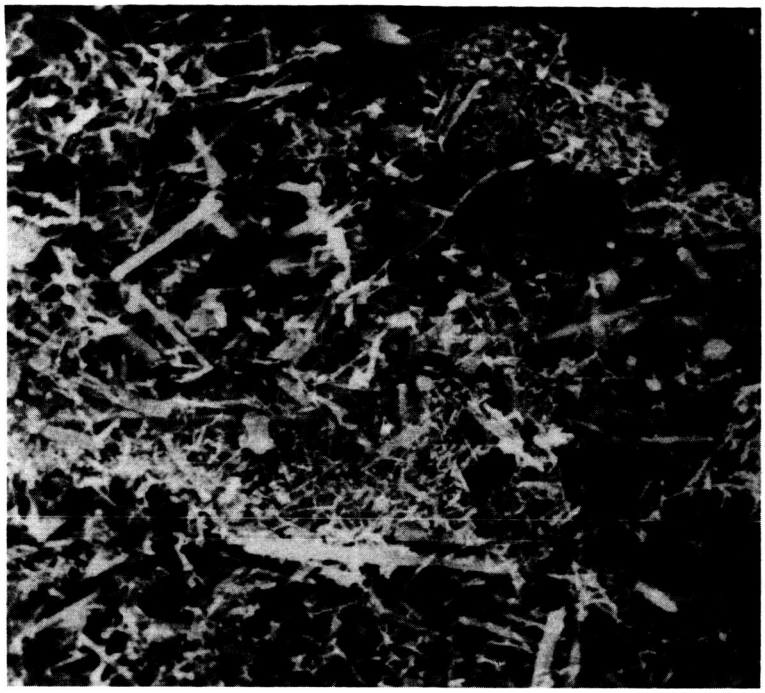
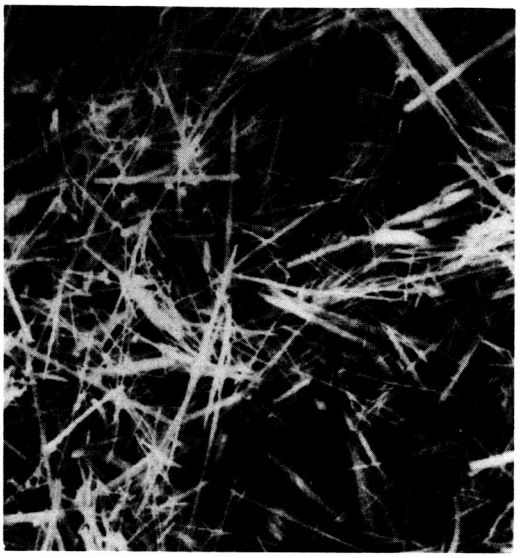


Figure 8. - Degraded water-leached material. X1000.

Figure 9. - Clusters of material from fibrous fraction. X1000.

(a) Chips. X800.



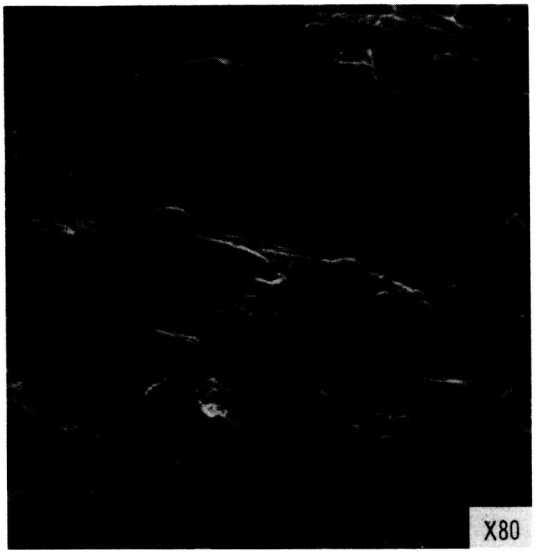
(b) Fibers. X800.

(c) Clusters. X800.

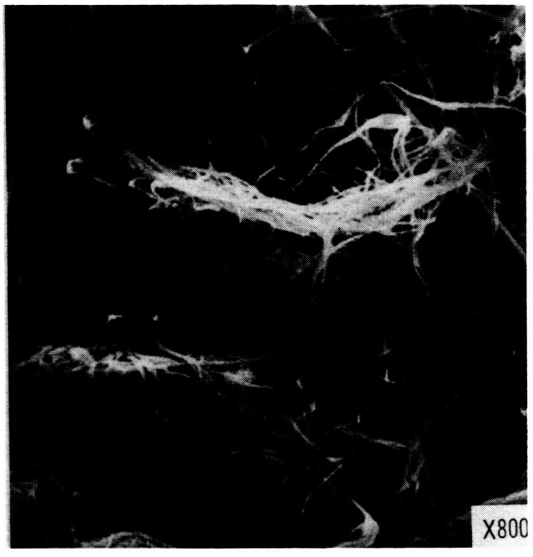
(d) Binding by colloid. X8000.

Figure 10. - Fractions from fibrous material.

Figure 11. - Clumps. X100.



Note cracks.



Note asbestos binding effect.

Figure 12. - Surface of potassium titanate-PTFE-asbestos composite matrix.

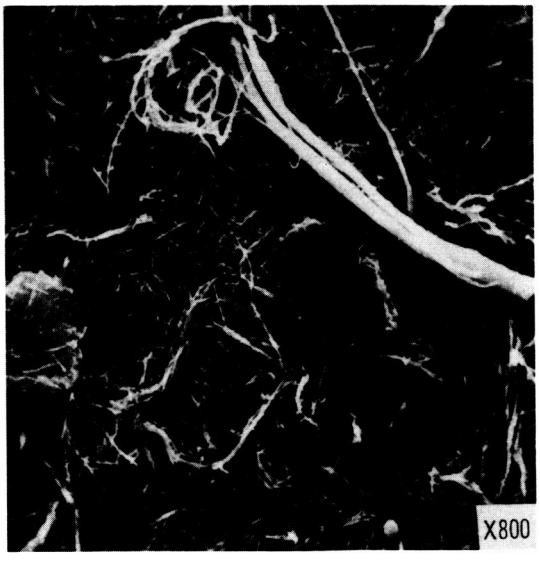
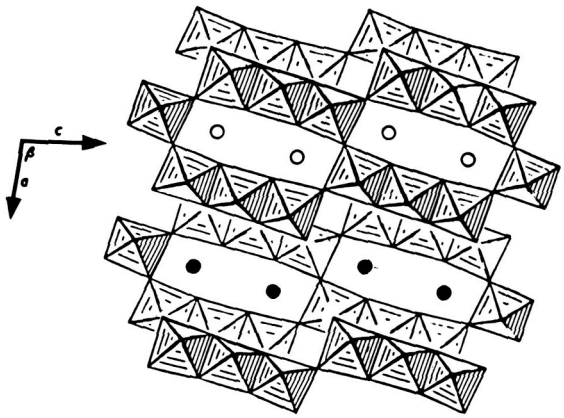
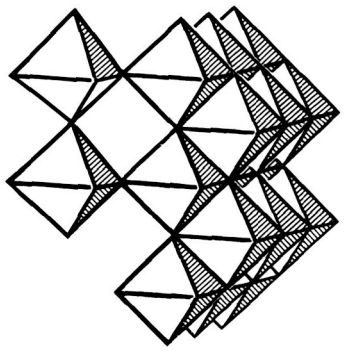


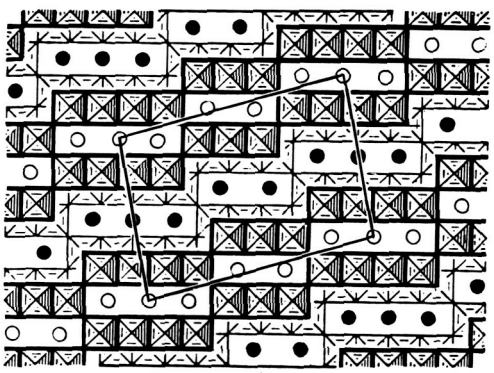
Figure 13. - Surface of asbestos matrix.



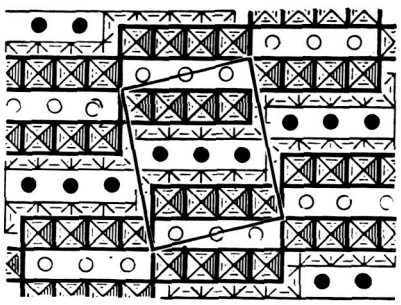
(a) Hexatitanate structure (ref. 8). View looking along fiber axis and down tunnels. Circles are alkali metal ion positions, filled in hexatitanate.



(b) Arrangement of octahedra in many titanates (ref. 8). View looking normal to fiber axis and tunnels. Aperture between isolated pair of octahedra and larger group is interconnection between tunnels in hexatitanate.

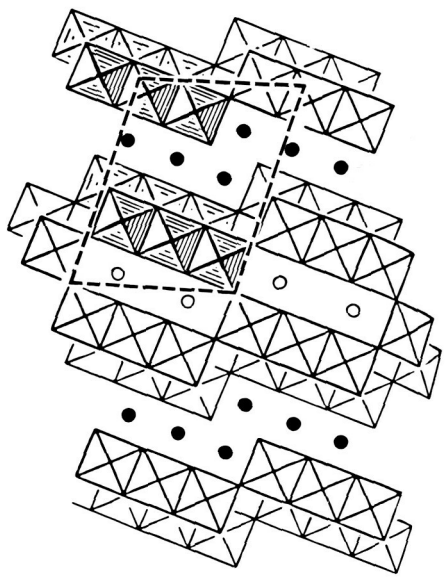


Heptatitanate



Octatitanate

(c) Heptatitnate structure (ref. 9) and postulated octatitanate structure. Viewed as in (a). Not all alkali metal ion positions are filled.



(d) Concept of tetratitanate structure (ref. 8). Hexatitanate ribbons alternate with trititanate ribbons. Note larger intertunnel access paths in transition regions.

Figure 14. - Crystal structures of alkali metal titanates (refs. 8 and 9). Courtesy of Sten Anderson, W. G. Mumme and the International Union of Crystallography.