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Impurity Control in Sapphire Whiskers

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The effect of selective chemical removal of impurity elements on the structure and high temperature stability of sapphire whiskers has been investigated. For Compagnie Thomson Houston (CTH) sapphire whiskers (with an "as-grown" impurity concentration of 6% silicon and approximately 2% (sodium + potassium + calcium)), treatment in a 20% H_2SO_4-20% HF solution (Solution A) effectively removed the grown-in second phase particles and formed a surface reaction product. The reaction product could be removed from the whiskers with distilled water and the "cleaned" whisker annealed at 1100°C for 17 h (in high purity argon) without attendant whisker disintegration. A similar effect was noted for Thermokinetic Fibers Inc. (TFI) whiskers (approximately 0.2% silicon) after treatment in Solution A. In both cases the improvement in high temperature stability is correlated with a reduction in silicon concentration to $< 0.15\%$.

An alternative treatment in H_3PO_4 (Solution B) resulted in preferential removal of (sodium + potassium + calcium) and aluminium from CTH whiskers. The grown-in second particles were retained in the whiskers and coarsened into a variety of configurations during an 1100°C/17 h anneal, which may be attributed to the geometry produced by differential whisker thinning.

1. Introduction

A previous investigation [1] demonstrated the effects of high temperature annealing on the structure of sapphire whiskers. In Compagnie Thomson Houston whiskers (designated CTH) containing 6% silicon and approximately 2% (sodium + potassium + calcium), the second phase particles, which were present in the "as-grown" condition, coarsened during anneals at temperatures above 1000°C and resulted, eventually, in whisker disintegration. The activation energy for diffusion of the impurity ion(s) was established, but the particular species involved could not be directly identified. Some evidence for the major role of silicon was provided by experiments on Thermokinetic Fibers Inc. whiskers (designated TFI) which contained a relatively low level of silicon (0.2%), as there were practically no second phase particles in the "as-grown" condition, but the comparison was complicated by the presence of continuous second phase coatings on some whiskers.

The objective of the present experimental series has been to investigate the effects of removal of impurity from the CTH and TFI whiskers, both on the "as-grown" structure and on the structure after exposure to a temperature of 1100°C. Two main types of experiments were attempted, namely, first, to remove all the impurity elements from the whiskers and, second, to remove particular elements selectively from the whiskers. In practice, it was found that the selective removal of particular elements could not be performed in the ideal manner, but a sufficient variation in impurity level was obtained to effect a reasonable evaluation of the relative contributions. In this manner, it has been possible to identify the impurity producing disintegration, with the benefit that the conditions necessary for high temperature structural stability of sapphire whiskers have been more clearly defined.

2. Experimental Procedure

Sapphire whiskers obtained from Compagnie Thomson Houston (CTH) and Thermokinetic Fibers Inc. (TFI) were examined by the replication technique described previously [1]. The conditions examined for both CTH and TFI whiskers were:

(*a*) "As-grown" for control.

(*b*) After 120 h in 20% HF 20% H_2SO_4 (Solution

TABLE I Semi-quantitative spectrographic analyses of CTH and TFI whiskers

Element	CTH			TFI		
	"As-grown" %	Solution A %	Solution B %	"As-grown" %	Solution A %	Solution B %
Si	6.0	0.15	10.0	0.2	0.07	0.05
Na + K	1.7	—	0.75	—	—	—
Ca	0.2	0.01	0.02	0.01	0.02	0.002
Fe	0.12	0.35	1.0	0.01	0.07	0.04
Mg	0.15	0.06	0.15	0.01	0.04	0.02

A), which is a development of the solution used by Calow and Moore [2] for whisker etching.
(*c*) After treatment in Solution A and an anneal at 1100°C for 17 h in high purity argon.
(*d*) After treatment in Solution A and 24 h in distilled water.
(*e*) After treatment in Solution A, 24 h in distilled water and an anneal at 1100°C for 17 h in high purity argon.
(*f*) After treatment in concentrated H_3PO_4 (Solution B), which was used for chemical polishing of sapphire whiskers by Brenner [3] and Bayer and Cooper [4].

3. Results

3.1. Chemical Analysis

The effects of treatment in Solution A and B on the composition of the whiskers are shown in table I. It can be seen that, in general. Solution A reduces the silicon and (sodium + potassium + calcium) to a low level, while not removing the iron. In contrast, Solution B produced a partial removal of (sodium + potassium + calcium), while silicon and iron actually appeared to increase (this is probably due to its selective removal of aluminium oxide).

3.2. Electron Microscopy

3.2.1. CTH whiskers

The structure of a typical "as-grown" CTH whisker, containing a number of second phase particles is shown in fig. 1. The diameter (d) of the second phase in different whiskers varied from approximately 0.2 to 1.1 μm. An examination of the whisker morphology after treatment in Solution A revealed particles of a reaction product on the surface of the whisker, as shown in fig. 2. It can be seen that the reaction product was associated with both large and small whiskers. The reaction product was both attached to the whiskers and also in a detached state. It was not possible to detect any "grown-in"

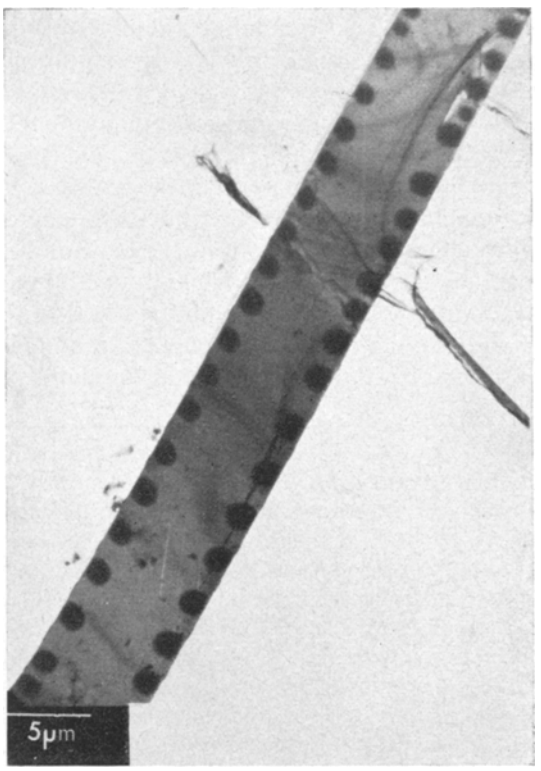


Figure 1 An "as-grown" CTH whisker with second phase particles.

second phase particles in the whiskers after treatment in Solution A. Fig. 3 is a higher magnification view of the reaction product and shows the generally square configuration with an approximate mean width of 0.4 μm and a mean density of approximately 2.4 particles/μm^2.

Whiskers treated in Solution A were annealed at 1100°C for 17 h in high purity argon. The effect of this treatment on the "as-grown" whiskers (i.e. without Solution A treatment) was to produce considerable coarsening of the second

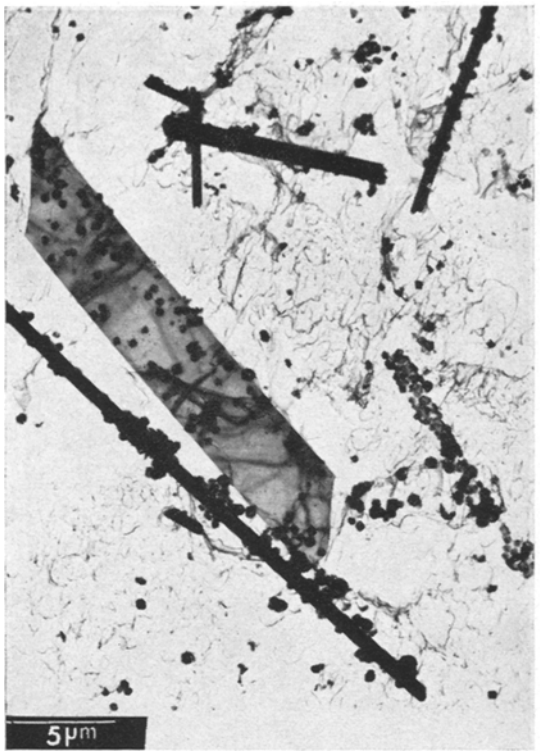


Figure 2 CTH whiskers after 120 h in Solution A.

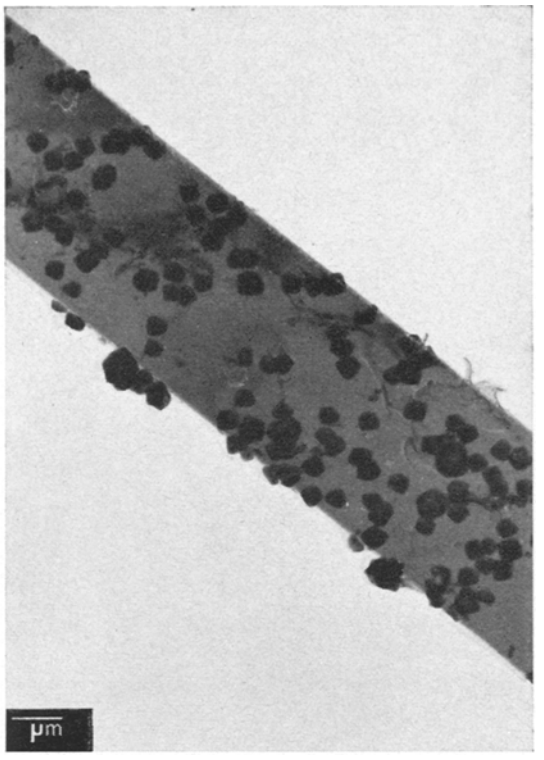


Figure 3 A CTH whisker with the reaction product formed after 120 h in Solution A.

phase particles (the average diameter increasing to approximately 2.5 μm as shown in fig. 4). In contrast, subjecting the "Solution A treated" whiskers to a similar anneal produced an interaction between the reaction product and the whisker, as shown in fig. 5. It can be seen that the reaction product has developed an irregular shape and is attached firmly to the whisker. The larger whiskers remained coherent, but it can be seen that breakdown of some of the small whiskers has occurred with debris formation. The "embedding" of the reaction product in the whiskers is shown more clearly in fig. 6.

As an alternative treatment the removal from the whiskers of the Solution A reaction product was attempted. It was found that leaving the whiskers in distilled water for 24 h effectively removed the reaction product, as shown in fig. 7. The whiskers observed after this treatment, as shown in fig. 7, appear regular in outline.

Annealing the "Solution A treated" and washed whiskers at 1100° C for 17 h produced no disintegration of the whiskers, as shown in fig. 8.

One method of reducing the amount of

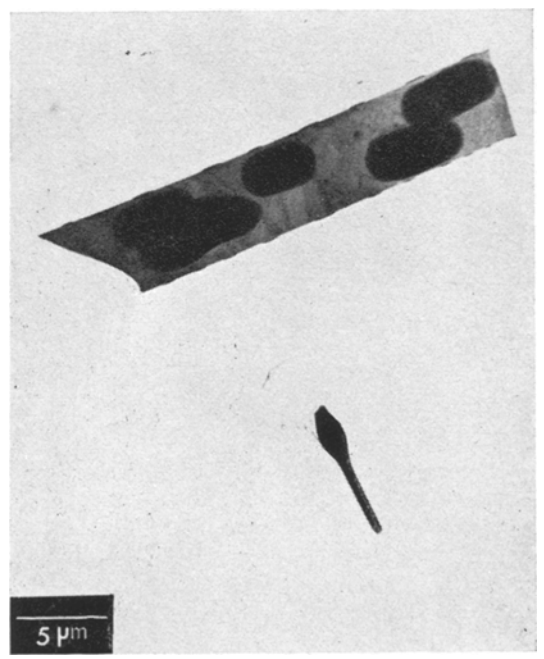


Figure 4 An "as-grown" CTH whisker after an anneal at 1100° C for 17 h.

Figure 5 "Solution A treated" CTH whiskers after an anneal at 1100° C for 17 h.

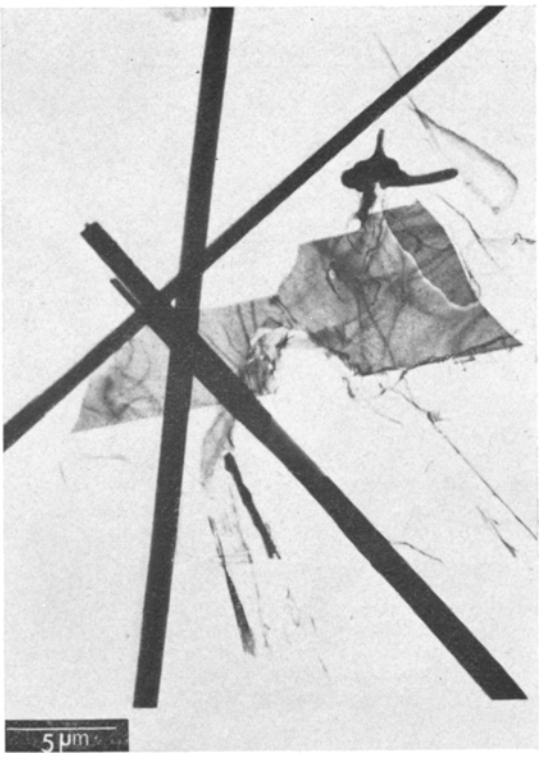


Figure 7 CTH whiskers after treatment in Solution A followed by washing in distilled water.

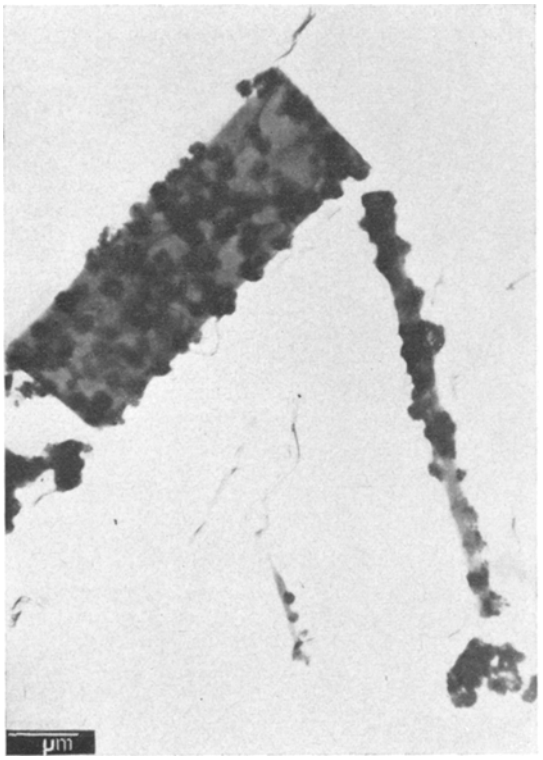


Figure 6 "Embedding" of the reaction product on "Solution A treated" CTH whiskers after an anneal at 1100° C for 17 h.

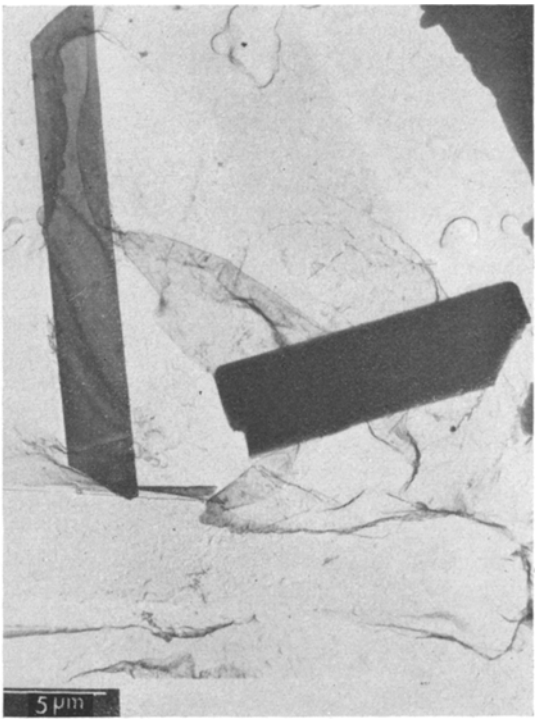


Figure 8 CTH whiskers after Solution A treatment, water washing, and an anneal at 1100° C for 17 h.

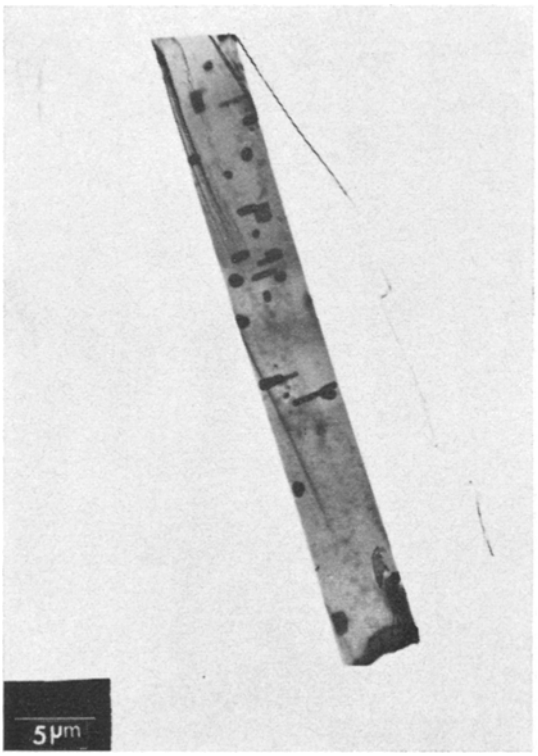


Figure 9

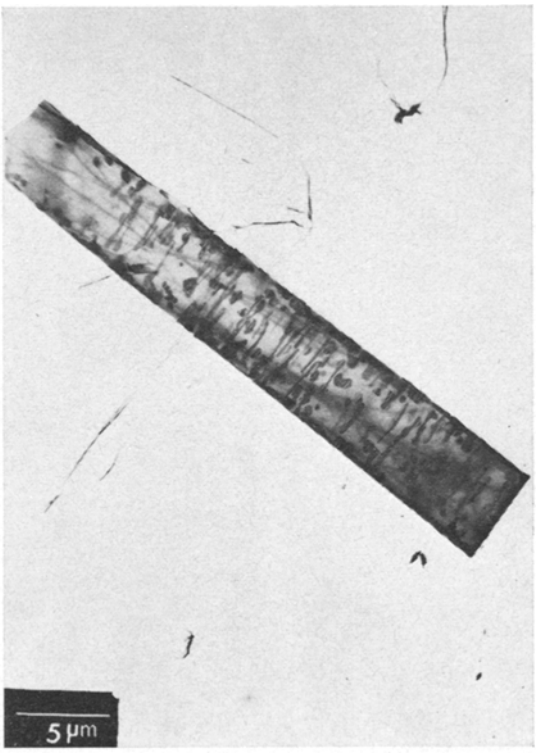


Figure 10

Figures 9 and 10 CTH whiskers after a shorter treatment in Solution A (72 h) and an anneal at 1100° C for 17 h.

impurity element removed from the whiskers is obviously by decreasing the time in Solution A. It was found that on reducing the time to 70 h, only a few examples of a reaction product were detected, which exhibited a more crystallographic morphology (figs. 9 and 10) after a 1100° C anneal.

Treatment of whiskers in Solution B produced some changes in the shape of the sapphire whiskers. Fig. 11 shows an example of a whisker which was reduced non-uniformly in width and thickness. This effect is further demonstrated in the whisker in fig. 12, in which there is both a variation in thickness and rounding of the end of the whisker. However, treatment in Solution B did not remove the second phase particles and annealing whiskers treated in this manner at 1100° C for 17 h produced changes similar to those noted for the "as-grown" whiskers. As shown in fig. 13 particle coarsening occurred in some whiskers although on a finer scale than previously noted [1]. Other second phase configurations were also noted, such as the irregular particles shown in fig. 14 together with a distinctive two column or "duplex core" second phase region. This duplex core feature of the structure was found to be a characteristic one and is further demonstrated in fig. 15.

3.2.2. TFI whiskers

Treatment of the TFI whiskers in Solution A produced a reaction product (fig. 16), similar in appearance, but on a much finer scale than that noted on the CTH whiskers, with an average width of approximately 0.15 μm and an average density of approximately 10 particles/μm^2. The reaction product became embedded in the whiskers during an anneal at 1100° C for 17 h in a similar manner to the effect described for the CTH whiskers. The reaction product could also be completely removed by water washing, after which it was possible to anneal the whiskers at 1100° C without producing any structural change (fig. 17).

Treatment of the TFI whiskers in Solution B did not produce any second phase effects such as noted in CTH whiskers.

4. Discussion

From the results it is possible to identify the

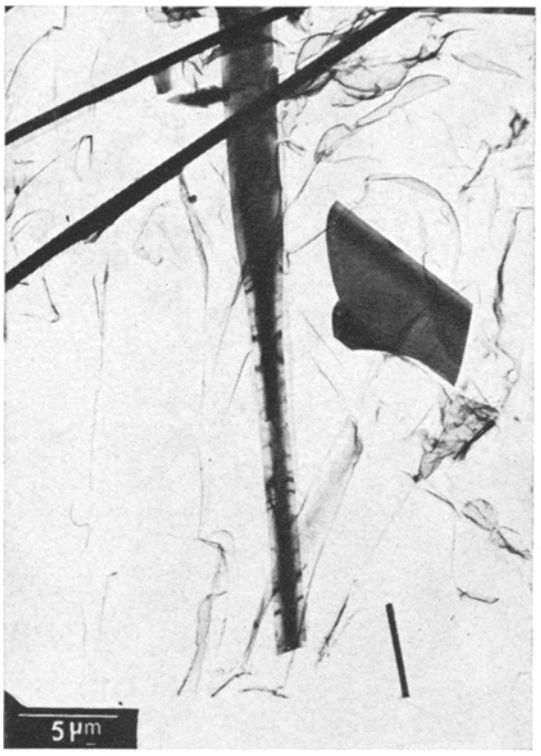


Figure 11

Figure 12

Figures 11 and 12 CTH whiskers after treatment in Solution B for 120 h at 60°C.

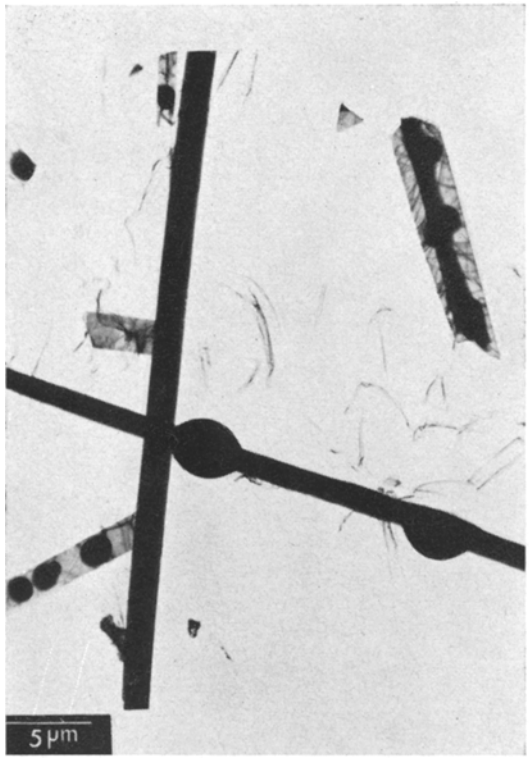
impurity element contributing to whisker breakdown. Treatment with Solution A resulted in the formation of a reaction product on the surface of both CTH and TFI whiskers. In the case of the CTH whiskers the silicon and (sodium + potassium + calcium) impurities were reduced to a low level, while for the TFI whiskers the silicon impurity only was removed (there being a negligible concentration of (sodium + potassium + calcium). The reaction products appeared similar, as both were water soluble and both reacted with the respective whiskers during a 1100°C anneal. Hence, it is likely that the reaction product contains the same impurity (i.e. silicon) in both cases. With the removal of the reaction product from the whisker surface by water washing, it was possible to anneal both CTH and TFI whiskers at 1100°C/17 h without any significant second phase coalescence or whisker breakdown taking place. Hence it is concluded that for the whiskers to remain stable at 1100°C, the silicon concentration must be $\leq 0.15\%$. A measure of the amount of reaction product in each case can be determined on an area basis by the product of the number of particles per unit area and the average particle area. This yields the following:

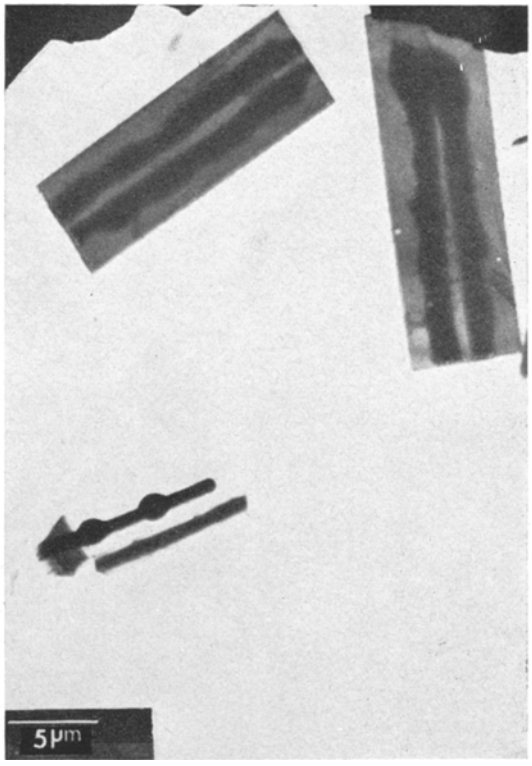
For CTH whiskers, total reaction product area = 0.32 μm^2 per μm^2 of whisker

For TFI whiskers, total reaction product area = 0.23 μm^2 per μm^2 of whisker.

Such an estimate is only approximate, as it does not take into account the particles which became detached from the whiskers, but the greater amount of reaction product on the CTH whisker is certainly consistent with the larger silicon concentration in the CTH whiskers.

Further confirmation of the detrimental effect of silicon, rather than (sodium + potassium + calcium) is provided by the results obtained in Solution B. This did not reduce the silicon content in CTH whiskers and, in fact, there was an apparent increase in silicon concentration which was probably due to the removal of aluminium. However, there was partial removal of the (sodium + potassium + calcium) group. After this treatment followed by an anneal at 1100°C for 17 h some of the features exhibited by the





Figures 13, 14 and 15 Various second phase configurations formed in "Solution B treated" CTH whiskers after an anneal at 1100°C for 17 h.

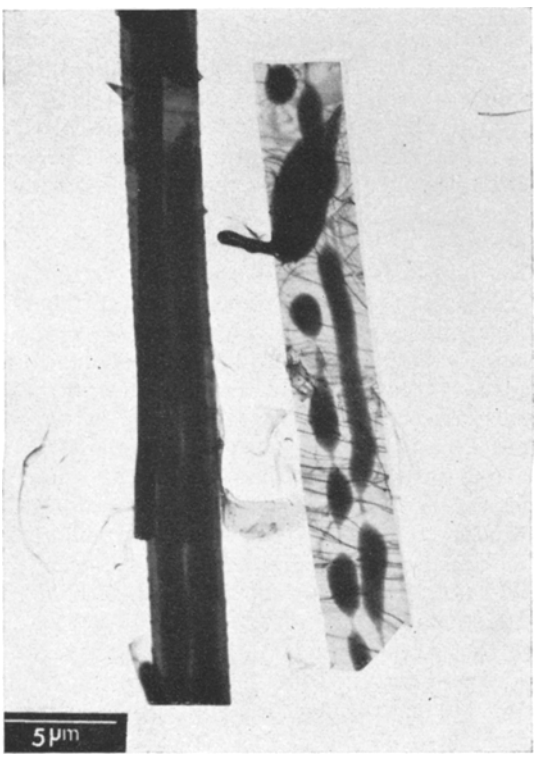


Figure 14

"as-grown" whiskers were observed, namely the coalescence of second phase particles and subsequent whisker breakdown.

There were also some differences in the form of the second phase developed after annealing the "as-grown" and "Solution B treated" whiskers. After treatment in Solution B, followed by an anneal at 1100°C for 17 h, many examples of second phase particles (or regions) were noted in CTH whiskers. In general there had been an increase in the size, and a decrease in the number, of the particles (or regions), but there was a variation in the morphology of the particles (or regions) between different whiskers. The four characteristic particle (or region) configurations observed were:

(*a*) Discrete, "round" particles (seen for example in the small whiskers in fig. 13) which resemble, and have a similar diameter of 1.2 to 2.0 μm to, the coalesced particles observed in as-grown whiskers after treatment at 1100°C for 8 h [1].

(*b*) A central "core" with spheroidal projections

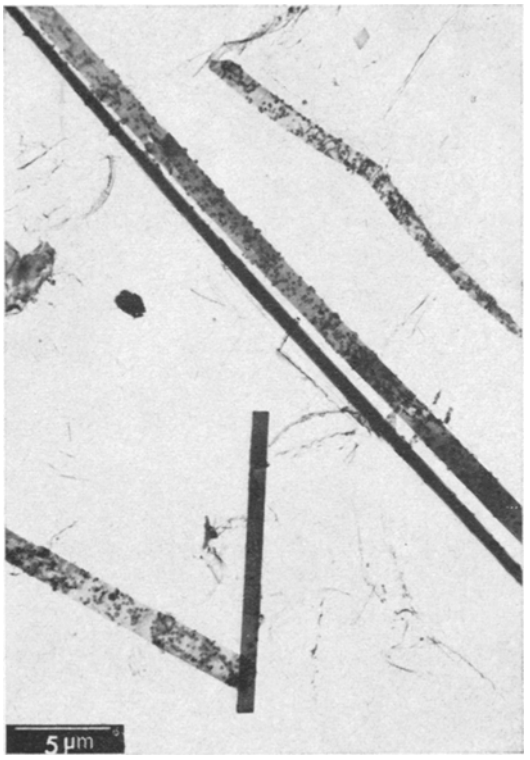


Figure 16 TFI whiskers after 120 h in Solution A.

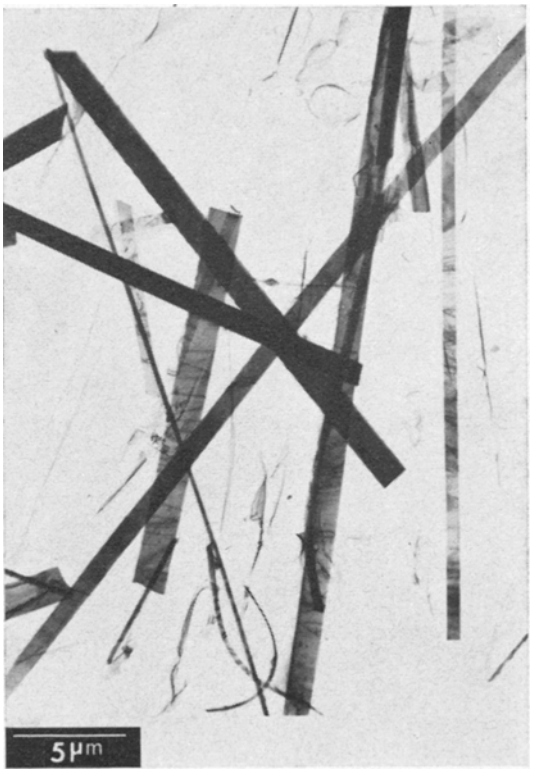


Figure 17 TFI whiskers after treatment in Solution A, water washing, and an anneal at 1100° C for 17 h.

of about the same dimension as the discrete particles, e.g. fig. 13.
(*c*) A duplex core with some periodic ovulation, but with no definite spheroidal projections, as seen in figs. 14 and 15.
(*d*) A series of irregular particles, which resulted from the break up of the central core.

Of these configurations, the duplex core (*c*) was the most common. This is in contrast to the position after treatment of the "as-grown" whiskers at 1100°C for 17 h, when condition (*a*), i.e. discrete particles, predominated (as shown in fig. 4). It should be noted that the discrete particles shown in fig. 13 are smaller than those in fig. 4 and correspond more nearly to the form noted after annealing the "as-grown" whiskers for 8 h rather than 17 h at 1100°C.

The particle coarsening noted after annealing the "as-grown" whiskers was attributed [1] to a resolution of the smaller particles and a reprecipitation on the larger particles, promoted by the attendant energy reduction and controlled by the Wagner volume diffusion theory [5]. This process occurred in a geometrically regular whisker (ribbon like or cylindrical). However, it is suggested that after treatment in Solution B the sapphire whisker is no longer geometrically regular, a factor which could effect the subsequent particle coarsening during annealing. For example, fig. 1 shows that the "grown-in" second phase particles are distributed towards the edges of the ribbon-like whisker. Hence, as Solution B, from the analysis (table I), removes Al_2O_3 preferentially to silicon, it is probable that the central portion of such whiskers is dissolved more rapidly and becomes thinner than the edges. Consequently, if the difference in thickness becomes large the ability of the second phase particles to coarsen by material transfer across the whisker is limited. Instead, material transfer probably occurs exclusively along the whisker, forming a duplex core, particularly as the particles are generally closer together in this direction. This argument will be investigated in more detail.

The other major impurity in both CTH and TFI whiskers is iron, but the present results indicate that this does not contribute to whisker breakdown during 1100°C anneals as treatment

in Solution A (which produces a stable whisker) did not produce any reduction in the iron concentration.

5. Conclusions

(1) Treatment of CTH and TFI sapphire whiskers in a 20% HF 20% H_2SO_4 solution (Solution A) for 120 h removes the "grown-in" second phase particles and forms a reaction product on the whisker surface.
(2) The reaction product is removed from both types of whisker by treatment in distilled water and the washed whisker can be annealed at 1100° C for 17 h without attendant disintegration.
(3) As the treatment in Solution A reduces the silicon concentration in both CTH and TFI whiskers to $\leq 0.15\%$, it is concluded that this represents the maximum permissible silicon concentration consistent with preventing whisker breakdown at high temperature.
(4) Treatment of CTH and TFI whiskers in H_3PO_4 (Solution B) does not remove the "grown-in" second phase particles, but preferentially removes the aluminium and (sodium + potassium + calcium) constituents.
(5) The "Solution B treated" whiskers exhibit four characteristic second phase configurations after an 1100° C/17 h anneal, the most prominent being a central duplex core region. It is suggested that this feature results from the whisker geometry produced by differential thinning in Solution B.

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