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Temperature Induced Structural Changes in Sapphire Whiskers

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The effect of high temperature annealing (800 to 1500°C) on the structure of individual sapphire whiskers has been determined with an electron microscope technique. Two types of whiskers, grown by a similar process, but containing different levels of silicon impurity (6 and 0.2% respectively) were studied. Discrete second phase particles were observed within and at the surface of many of the whiskers with 6% silicon. After heat treatments at 1000 to 1300°C in high purity argon, these particles coarsened and coalesced in the larger whiskers and spheroidised on the surface of the smaller whiskers. In addition, a dispersion of fine particles was formed in some whiskers free from "grown in" particles.

Some melting of the second phase occurred between 1000 and 1400°C, with an attendant disintegration of the whiskers. Although the sapphire whiskers with 0.2 silicon% did not contain second particles, some breakdown of the whiskers also occurred at about 1300°C, a process which is attributed to the presence, and melting, of a surface coating.

Surface pits were formed at temperatures above 1000°C, and became extensive at 1400 to 1500°C, particularly in the 6% silicon whiskers. It is considered that the surface pitting is a consequence of impurity diffusion and internal stress in the sapphire whiskers.

1. Introduction

Sapphire whiskers have several intrinsic advantages as a reinforcing material for a high temperature composite system, among which are chemical inertness in an oxidising environment, large elastic modulus and resistance to creep. However, for the effective use of sapphire in such a composite, it is also necessary that the whiskers should be chemically compatible with metals such as nickel, which provide potential matrix materials, over the desired operating temperature range. It could be argued that a limited chemical reaction between the whisker and matrix will improve the interfacial bonding, but certainly any continuous reaction, which will lead ultimately to whisker destruction, has obviously to be avoided.

This paper is concerned with a necessary prelude to a study of sapphire whisker-nickel compatibility, namely the determination of the effects of high temperature annealing on the structure of individual sapphire whiskers. Clearly it is essential to assess the nature of any morphological changes produced by such a process, particularly as the sapphire whiskers currently available contain a significant impurity level. For this reason two types of sapphire whiskers, one containing a relatively large amount of impurity (6% silicon and about 2% of other impurity elements) and the other being relatively pure (0.2% silicon), were selected for investigation.

2. Experimental Procedure

Sapphire whiskers were obtained from two sources, Compagnie Thomson Houston (Paris) (to be referred to as CTH whiskers) and Thermokinetic Fibers Inc. (USA) (to be referred to as TFI whiskers). Both types of whiskers were grown by the wet hydrogen process [1] but, as shown in table I, contained significantly different amounts of impurity.

The "as received" whiskers were prepared for electron microscope examination utilising the replication technique developed by Andrews [2]. This technique allows observation of the electron transmission images of the thinner whiskers, the silhouettes of the thicker whiskers, and the corresponding replicas of all the whisker surfaces. Other whiskers were annealed at 100°C incre-

ments in the range from 800 to 1500°C for various times up to 17 h, in high purity argon, before examination in a JEOL 7 electron microscope. Approximately 100 whiskers were examined in any particular condition in order to establish a reasonable level of reproducibility.

3. Results

3.1. CTH Whiskers (6% Silicon)

3.1.1. "As received" Whiskers

The width of the "as received" CTH whiskers measured in the electron microscope was from 0.2 to 10 μm (fig. 1). As the cross sectional configuration was found in general to be either cylindrical or ribbon like, this dimension could represent either the whisker diameter or one side of the ribbon. The width usually remained constant along the length of the whiskers, which ranged from 5 μm to several mm. The thinner whiskers (i.e. < 1 μm) were transparent to the electron beam, while for the thicker sections, examples of both transparent and opaque whiskers were noted. Selected area electron diffraction through the transparent whiskers revealed single crystal alumina patterns, which indicated that most of the whiskers were oriented parallel to an "a" direction.

Figure 1 Some "as received" CTH whiskers.

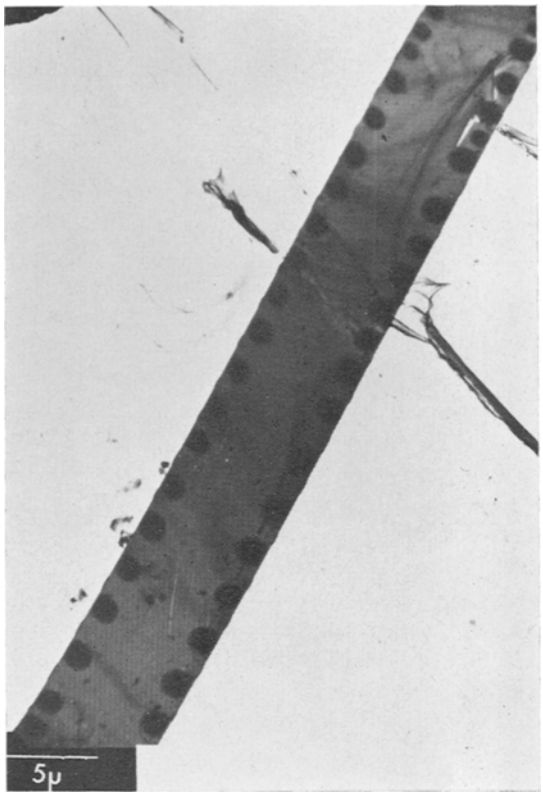


Figure 2 "Grown in" second phase particles (CTH whiskers).

Particles of a second phase were often noted in the whiskers and can be seen for example in the middle whisker in fig. 1. The particles tended to be regularly spaced (fig. 2) and were sometimes seen as projections in the corresponding surface replica. The second phase particles were always electron opaque and so could not be directly identified by selected area diffraction.

Annealing the "as received" whiskers at temperatures of 800 and 900°C, for times up to 17 h, produced no significant changes in the morphology of the "as received" whiskers. However, after heat treatments at or above 1000°C, several well defined effects were noted, which are described in the following sections.

3.1.2. Particle Coarsening

Coarsening of the existing "grown in" second phase particles was first observed in a few whiskers after an anneal at 1100°C, figs. 3 and 4

show typical whiskers after 2 h and 8 h respectively at temperature. It can be seen that the size of the particles increased and the number of particles per unit area decreased with increasing time. Some coalescence of the second phase particles can also be distinguished in fig. 4, and with longer annealing times (17 h) further examples of elongated particles which presumably resulted from the coalescence of initially "round" particles, were noted (fig. 5).

Annealing treatments at 1100°C also produced a change in the structure of some whiskers which had appeared free of "grown in" particles in the "as received" condition. As shown in figs. 6 and 7 a high density of small particles appeared in these whiskers after 2 h and 8 h at this temperature. (Comparing figs. 6 and 7 with figs. 3 and 4 it can be seen that these particles were more numerous and smaller than the "grown in" particles.) There was also some evidence for the formation of the small second phase in whiskers which did contain "grown in" particles (fig. 8).

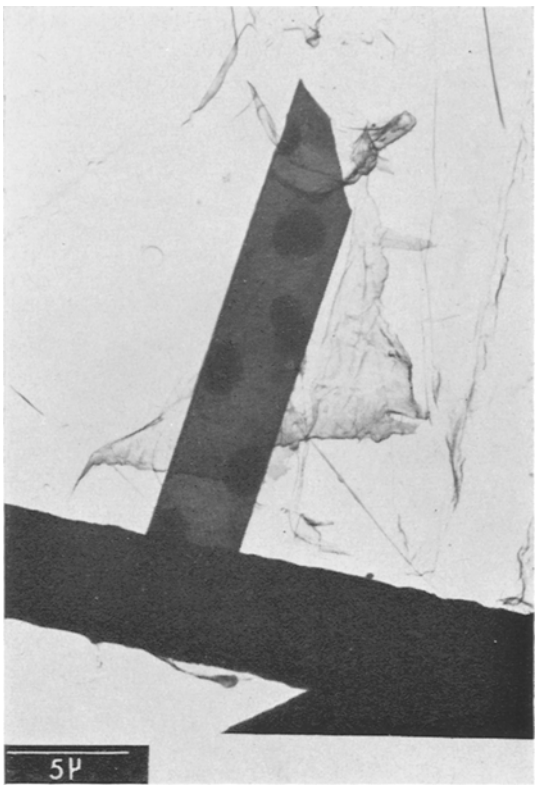


Figure 4 "Grown in" second phase particles (CTH whiskers) after 8 h at 1100°C.

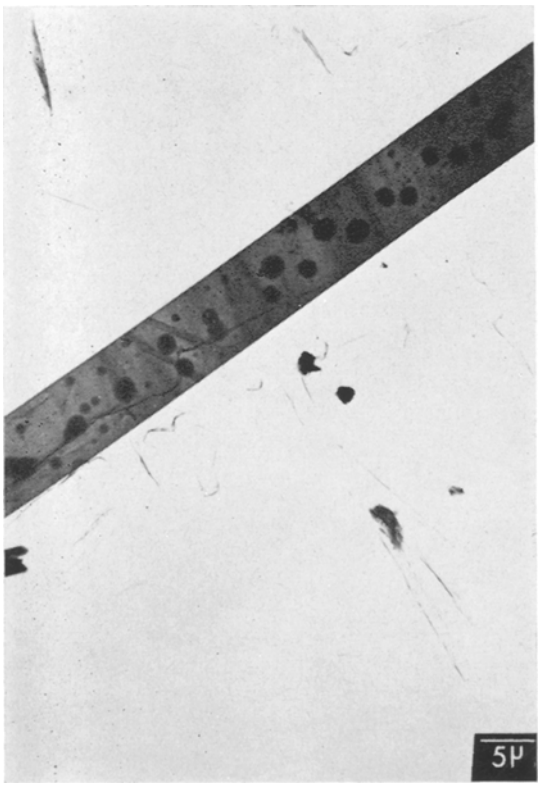


Figure 3 "Grown in" second phase particles (CTH whiskers) after 2 h at 1100°C.

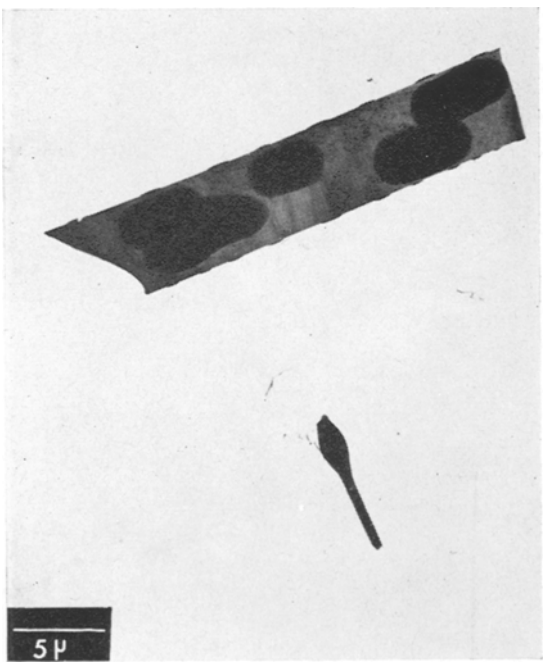


Figure 5 "Grown in" second phase particles (CTH whiskers) after 17 h at 1100°C.

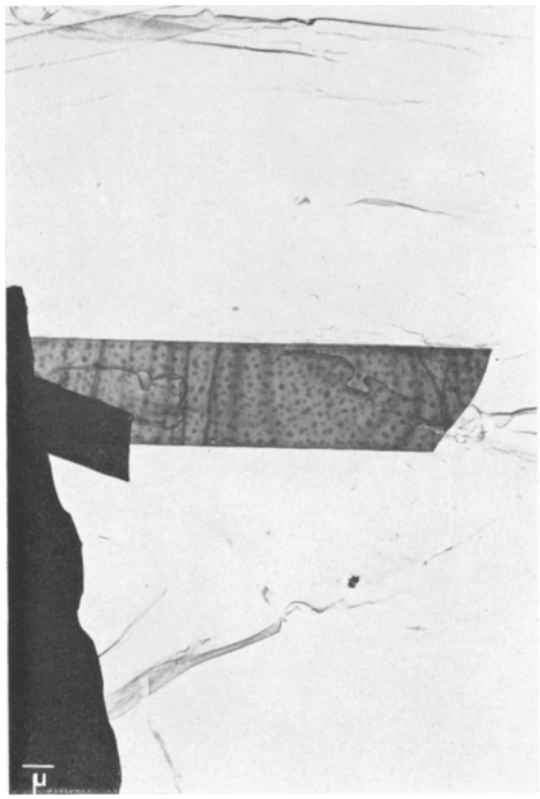


Figure 6 "New" second phase particles (CTH whiskers) after 2 h at 1100°C.

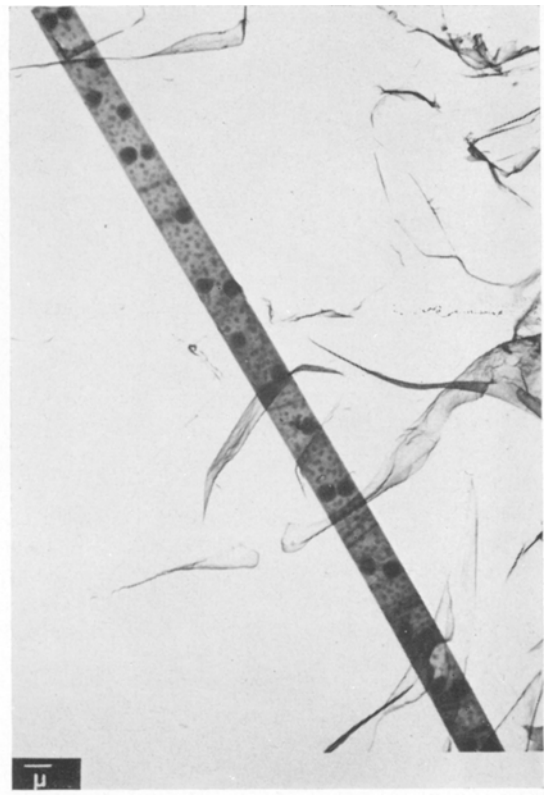


Figure 8 "Grown in" and "new" second phase particles (CTH whiskers) after 8 h at 1100°C.

Figure 7 "New" second phase particles (CTH whiskers) after 8 h at 1100°C.

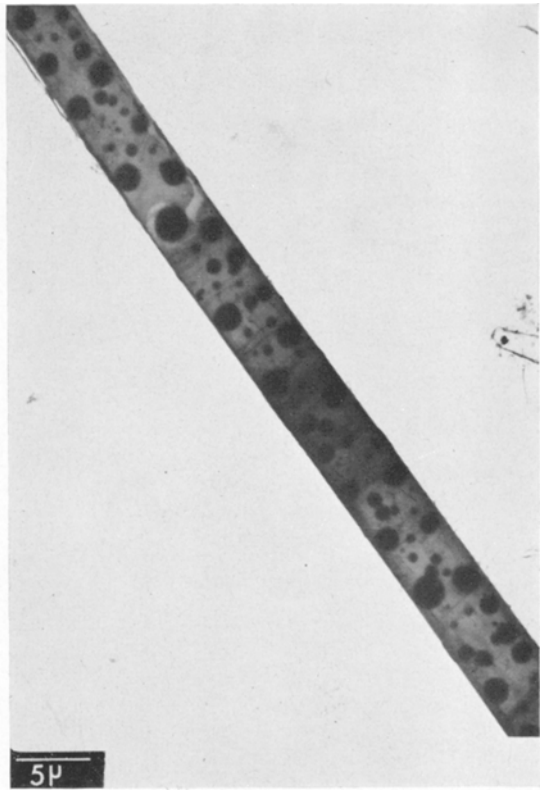


Figure 9 "Grown in" particles (CTH whiskers) after 2 h at 1300°C.

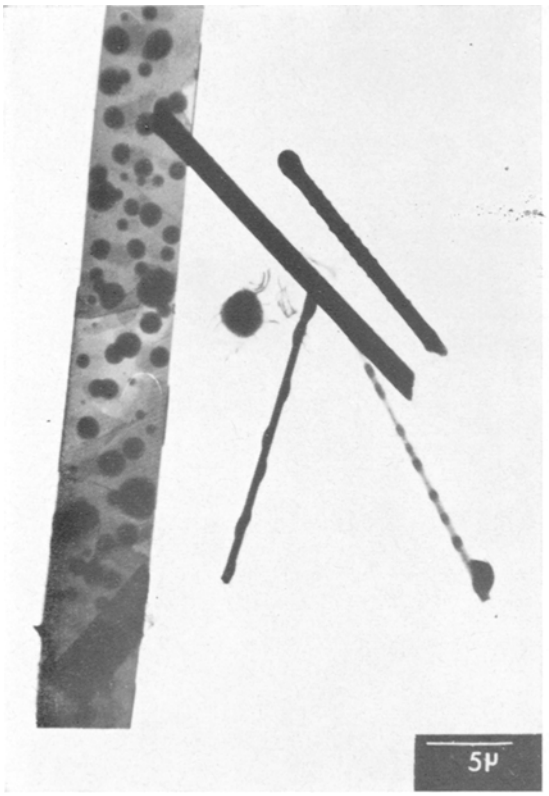


Figure 10 "Grown in" particles (CTH whiskers) and spheroidisation after 4 h at 1300° C.

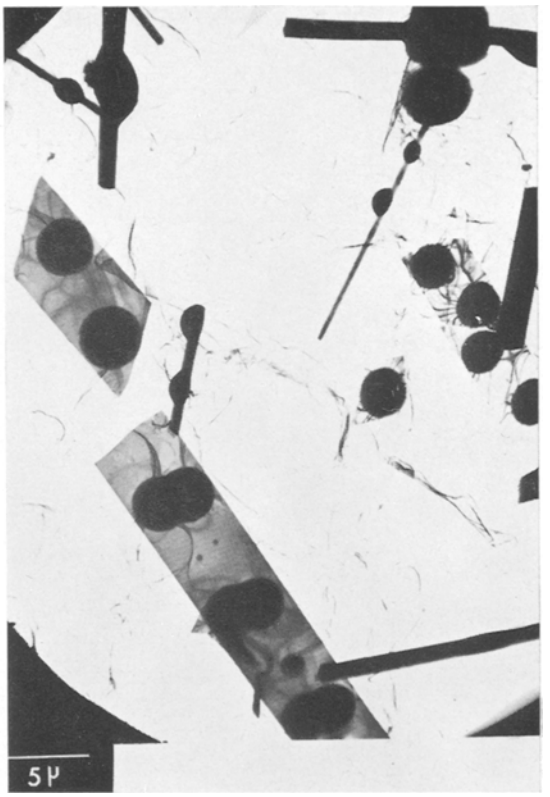


Figure 11 "Grown in" particles and spheroidisation (CTH whiskers) after 17 h at 1300° C.

Raising the annealing temperature to 1300° C produced a generally similar coarsening of the "grown in" particles to that observed at 1100° C, figs. 9, 10, 11 show the structure noted after 2, 4 and 17 h respectively. However, a major difference from the lower temperature results was the appearance of a diffusion zone around some particles and the resultant formation of a surface step (figs. 12, 13, 14). In addition the formation of the small particles (figs. 6, 7) was not detected.

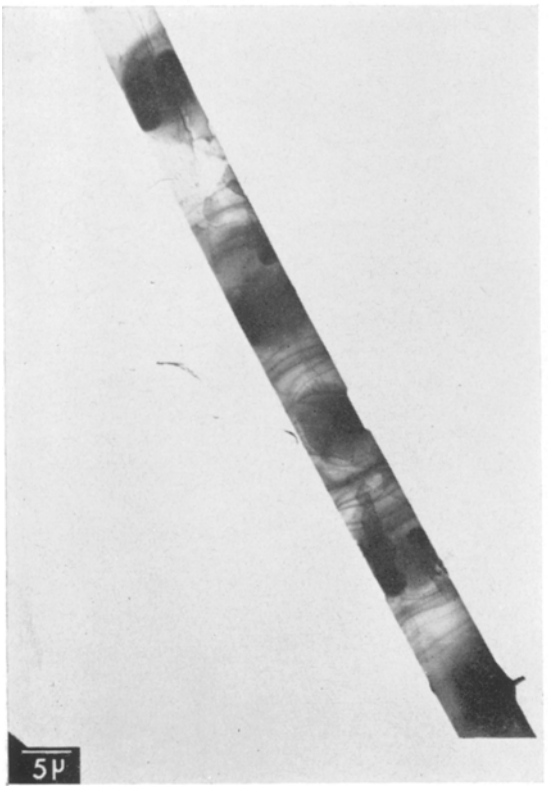
The effects of the various temperatures and times on the particle size and distribution described above, are brought together in table II. As the whisker thickness is not precisely known, all the estimates have been made on an area basis.

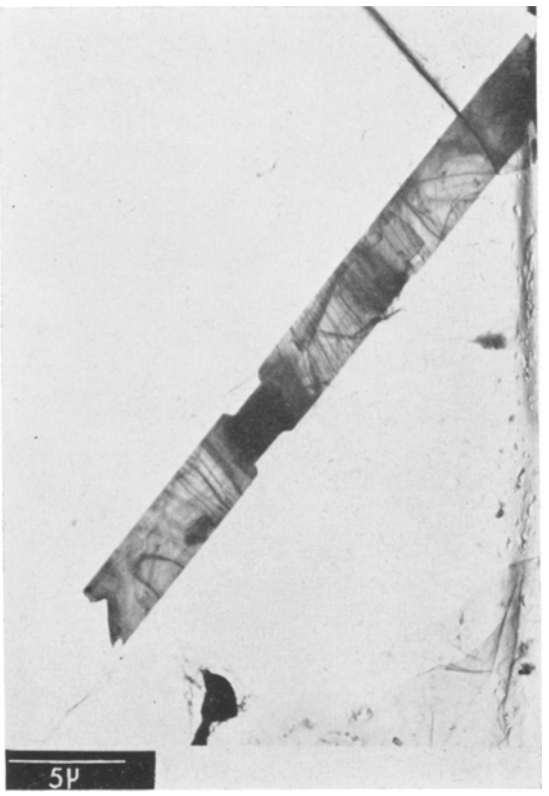
With further increases in the annealing temperature to 1400 and 1500° C, no examples of whiskers with second phase particles were observed after 4 h at these temperatures.

3.1.3. Spheroidisation

An effect relating to particle coarsening was observed in the smaller whiskers after heat treatments at, or above, 1000° C. However, it appeared to take place on the surface and resulted in the formation of a series of regularly spaced spheroidal projections of second phase, as shown in fig. 15. Spheroidisation was first noted after treatment at 1000° C for 17 h and became widespread after similar treatment at 1100° C. Examples of spheroidised whiskers were also noted after 1300° C anneals (see figs. 10, 11, for example), but no spheroidised whiskers were observed after a 1400° C or higher temperature heat treatment.

Subsequent to the establishment of spheroidisation of small whiskers after annealing, a careful scrutiny of the "as received" whiskers also revealed the presence of a *few* spheroidised whiskers.





Figures 12, 13, 14 Diffusion zone and surface steps (CTH whiskers) after 8 h at 1300° C.

Fig. 14

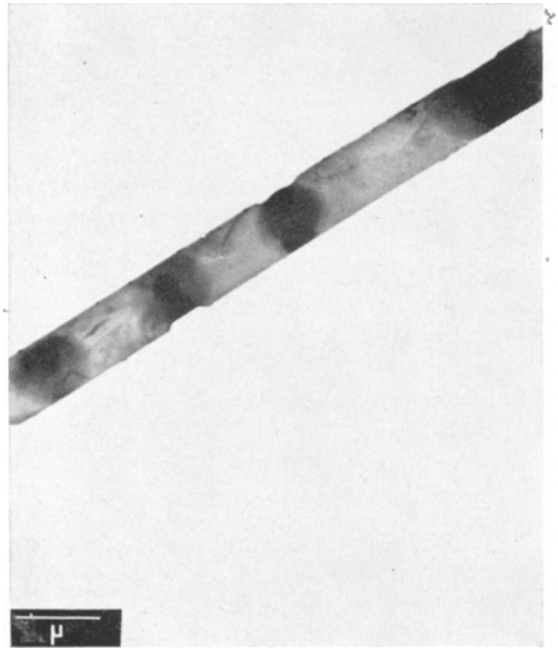


Fig. 13

Figure 15 Spheroidisation (CTH whiskers) after 17 h at 1100° C.

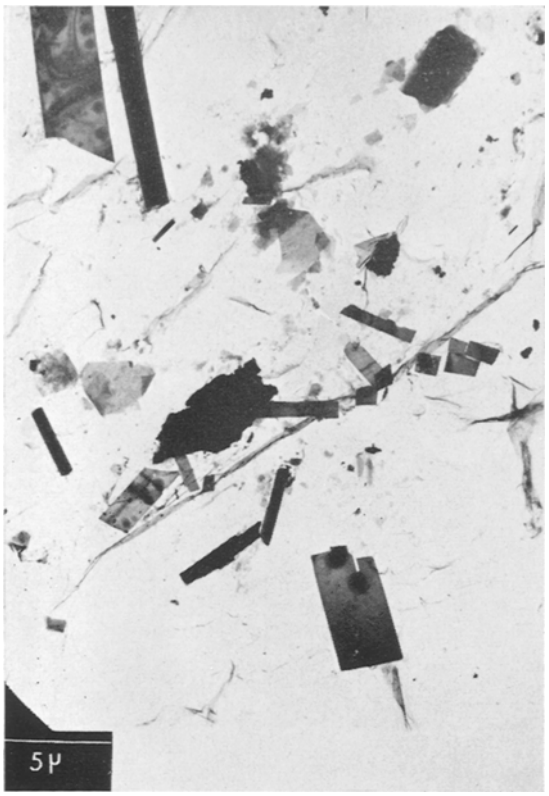


Figure 16 CTH whisker fragmentation after 4 h at 1300° C.

3.1.4. Disintegration

Whisker breakdown, which became apparent after annealing treatments above 1000° C occurred in several ways. Some whiskers containing second phase particles fragmented into shorter lengths, as shown in fig. 16, while a considerable number (estimated as 30%) disintegrated completely, leaving a fine debris (similar to that illustrated in fig. 21).

Another factor probably contributing to breakdown was the surface steps associated with second phase particles described in section 3.1.2. There was also evidence of holes in some whiskers (fig. 17) which presumably resulted from the separation of second phase particles. At higher annealing temperatures (1400 to 1500° C) extensive surface attack was noted and large hemispherical pits formed in the whiskers (fig. 18).

3.2. TFI Whiskers (0.2% Silicon)

The TFI whiskers were similar in size to the CTH whiskers, but a greater percentage were electron opaque and only a few contained discrete second phase particles. A major difference was that several "combined whiskers" and many tapered whiskers, as shown in fig. 19 were present in the TFI samples.

There was no evidence for second phase coalescence and only one example of spheroidisation was observed in the TFI whiskers after heat treatment at 1100° C. However, after a 1200° C anneal some whiskers did exhibit a surface spheroidisation effect, but as shown in fig. 20, on a much reduced scale compared with that noted in the CTH whiskers.

In spite of the apparently small amount of second phase present, a considerable amount of whisker debris was seen after a 1300° C anneal. Fig. 21 illustrates this point and shows a whisker which had almost disintegrated.

The coherent whiskers remaining after a 1300° C, or higher temperature anneal, were nearly always transparent as shown in fig. 22, which suggests that the breakdown is confined to the opaque specimens. It should be noted that the opaque whiskers in fig. 22 have an irregular "globular" outline.

Fragmentation of the whiskers into shorter lengths was not observed in the TFI whiskers. Occasional surface pits were noted on some whiskers after heat treatments above 1000° C

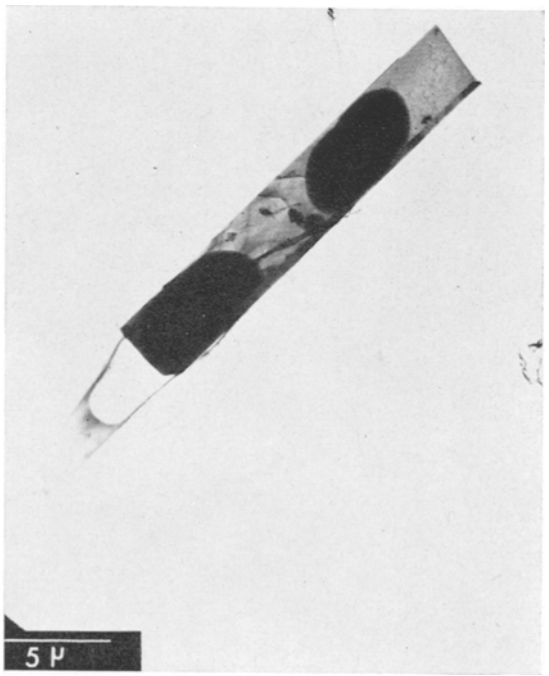


Figure 17 CTH whisker "hole" after 17 h at 1100° C.

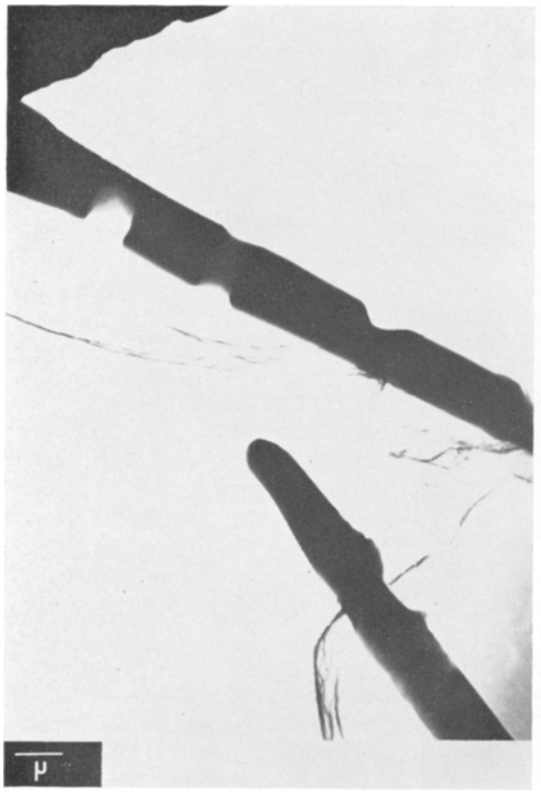


Figure 18 Surface pits (CTH whiskers) after 4 h at 1500°C.

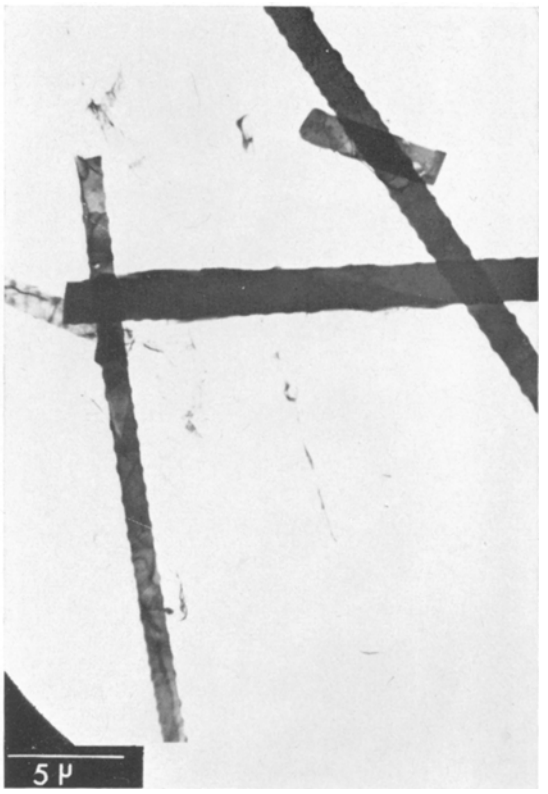


Figure 20 Surface spheroidisation (TFI whiskers) after 4 h at 1200°C.

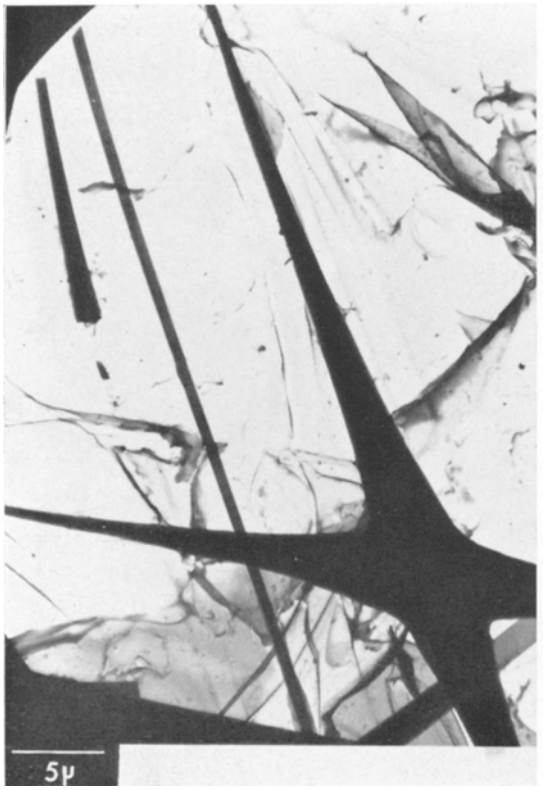


Figure 19 "As received" TFI whiskers.

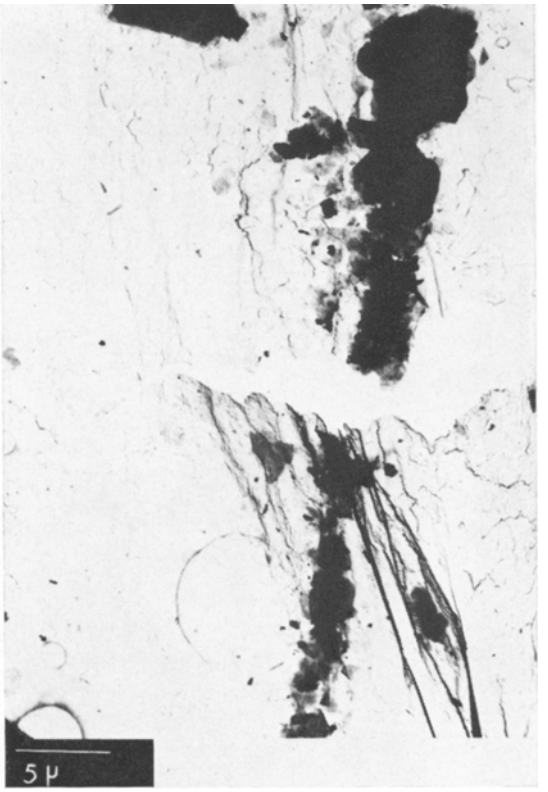


Figure 21 Whisker (TFI) debris after 17 h at 1300°C.

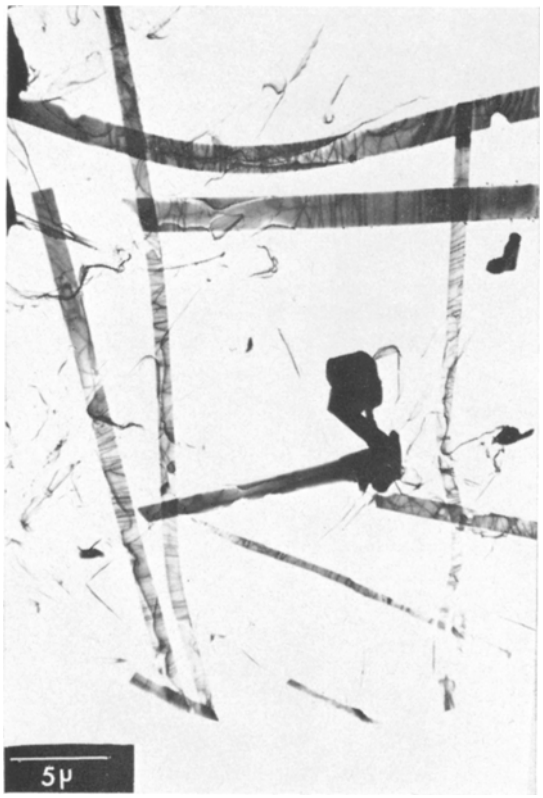


Figure 22 Coherent whiskers (TFI) after 4 h at 1400° C.

(fig. 22), but at any given temperature the extent of the pitting was less than that in the CTH whiskers.

4. Discussion

The present results demonstrate the considerable influence of impurity on the high temperature structural stability of sapphire whiskers and indicate that, for the CTH 6% silicon whiskers, the effects of impurity can be conveniently classified in three ranges of temperature, namely 0 to 900°C, 1000 to 1300° C and 1400 to 1500° C. In the "as received" condition the presence of second phase particles revealed that the impurity was not homogeneously distributed throughout the whisker. As the area fraction of the particles (~ 20%) was larger than the total impurity content (~ 8%), they are likely to contain Al_2O_3 as well as the various impurity elements listed in table I. The "circular" appearance of the particles suggests that the second phase is glassy rather than crystalline.

TABLE I Semi-quantitative spectrographic whisker analyses

	TFI whiskers (%)	CTH whiskers (%)
Si	0.2	6.0
B	—	0.015
Fe	0.015	0.12
Mg	0.015	0.15
Mn	<0.001	0.001
Ga	—	0.001
Be	—	0.004
Ti	0.003	0.03
Cu	<0.001	0.001
Na	—	0.7
Ni	0.001	0.003
Ca	0.01	0.2
K	—	1.0
Sr	—	0.005
Cr	0.001	0.004
V	—	<0.002
Ba	—	0.01

The "as received" structure was not affected by anneals up to 900° C, from which it is concluded that there was negligible diffusion of the impurity within this temperature range (for times up to 17 h). However, anneals in the range from 1000 to 1300° C produced an increase in the size of the "grown in" particles and a reduction in

TABLE II Second phase particle coarsening

Temperature (° C)	Time (h)	Diameter (μm) Minimum	Maximum	Average	No. of particles per cm³
"As received"	0	~0.2	1.4	0.7	5.0×10^7
1100	2	,,	2.0	1.1	3.6×10^7
	8	,,	2.2	1.8	1.5×10^7
	17	,,	~3.7	~2.5*	5.8×10^6
1300	2	,,	2.1	1.0	3.2×10^7
	4	,,	2.4	1.2	2.8×10^7
	17	,,	~3.9	~2.5*	7.0×10^6

*Some particles interconnected and non-spherical.

the number of the particles per unit area. It seems reasonable then to ascribe this effect to the particle coarsening concept, in which the smaller particles redissolved and then diffused to, and precipitated on, the larger particles. Support for this notion is provided by the reduction in the number of small particles and the more uniform particle size produced with time at high temperatures, as shown in table II. An estimate of the activation energy (Q) for the initiation of particle coarsening and for the diffusion of the impurity ion(s) may be derived from the rate equation:

$$\log \frac{1}{t} = \log K - \frac{Q}{RT} \qquad (1)$$

in which t represents time, K a pre-exponential constant, R the gas constant and T absolute temperature. From the results we have $T = 900$, 1000, 1100 and 1300° C and $t = > 17$, 4, 2 and < 2 h respectively, which data are plotted in fig. 23 and give an approximate activation energy of 37 kcal/mole. The magnitude of the coarsening effect suggests that silicon ions, as the major impurity, must be involved in the diffusion process and this was confirmed by some preliminary X-ray microprobe analysis on the larger particles. It is likely that the Na and K ions also contribute, but their presence in the larger particles was not definitely established.

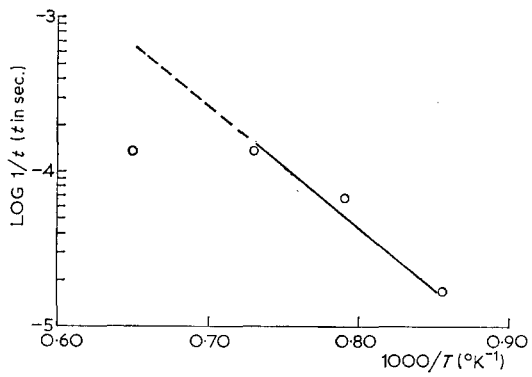


Figure 23 Activation energy for impurity ion(s) diffusion.

The mechanism of particle coarsening appeared to be growth of a sphere to a diameter, approaching half the width of the whisker, with further growth occurring by coalescence or elongation along the length of the whisker. In certain whiskers the latter process is probably promoted by the ribbon-like dimensions, with the width:thickness ratio of $\sim 5 : 1$. The relations between particle diameter, number of particles per unit area and time obtained in the experiments are plotted in fig. 24. The slopes obtained are in approximate agreement with the predictions of Wagner's theory [3] of particle coarsening by volume diffusion, which gives:

$$\bar{r}^3 \propto t$$
$$N_v \propto t^{-1} \qquad (2)$$

with $\bar{r}$ representing the mean particle radius and N_v the number of particles per unit volume, but a more detailed study is required to substantiate this finding. The dependence of particle size on temperature however is not that given by Wagner for diffusion of a particular ion species ($\bar{r} \propto 1/T$). This difference is probably due to the variation in impurity type and content between whiskers. Such an effect may also account for the nucleation of "new" particles in certain whiskers apparently free from "grown in particles".

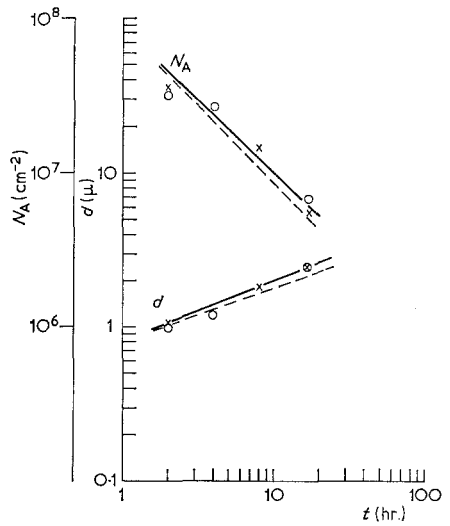


Figure 24 Relation between particle diameter (d), number of particles per unit area (N_A) and time (t). Discontinuous lines represent theoretical predictions, X 1100° C measurements and O 1300° C measurements.

It is interesting to note that spheroidisation on small whiskers takes place at about the same rate as particle coarsening. The likely difference between the two processes is that spheroidisation is accomplished by surface diffusion, while coarsening results largely from volume diffusion. Hence the similarity of the kinetics suggests that

there is little difference between surface and bulk diffusion in a material of whisker dimension.

The formation of surface steps associated with the growth of the second phase particles may be explained in terms of the rapid diffusion of the impurity ion(s) (with $Q \sim 37$ kcal/mole) relative to the matrix Al^{+3} and $O^{=}$ ions (with $Q = 152$ [4], 110 [4] and 114 [5] kcal/mole for $O^{=}$ in single crystal Al_2O_3, $O^{=}$ and Al^{+3} in polycrystalline Al_2O_3, respectively). Therefore the diffusion of the impurity ions to the second phase particles at 1300° C is not compensated by counter diffusion of Al^{+3} (taking the generally accepted notion of a relatively rigid oxygen framework). Consequently a large number of vacant sites are created adjacent to the particle, which lead to the formation of a surface step.

No particles were observed after anneals at 1400° C for 4 h or longer and from the evidence of whisker debris it is concluded that the particles have melted with a resultant disintegration of the whiskers. Some whisker debris was actually noted after all anneals above 1000° C, which suggests melting occurred over a range of temperature. Such a result is as expected from the variable impurity content of the whiskers. The values of temperature are also in good agreement with the SiO_2 corner of the K_2O–Al_2O_3–SiO_2 phase diagram [6] which has a boundary line linking eutectics at 985 and 1470° C.

The role of impurities in the TFI whiskers (0.2% Si) is an intriguing one, as they were nominally much purer than the CTH whiskers (see table I) and only a few "as received" whiskers contained second phase particles. However, the disintegration of many of the opaque whiskers after 1300° C heat treatment definitely appeared to be associated with a melting process (see, for example, the "globular" remnants in fig. 22).

This would suggest that these whiskers had a continuous surface coating of a second phase, which was responsible for the melting of the whiskers. One test of this hypothesis would be to remove the coating by a suitable chemical polishing technique. Such an experiment successfully demonstrated the existence of a second phase, as, after 67 h in hydrofluoric acid followed by an 1100° C anneal, a spheroidised discontinuous coating was noted (fig. 25). Therefore, it may be concluded that many of the opaque TFI whiskers have a continuous second phase coating.

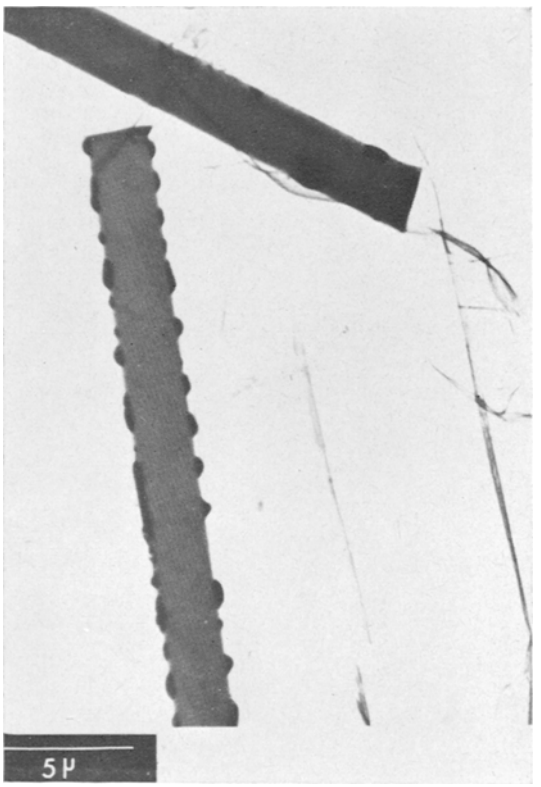


Figure 25 Spheroidisation (TFI whiskers) after 67 h in hydrofluoric acid and 17 h at 1100° C.

From table I the second phase associated with the TFI whiskers would probably consist of Al_2O_3 and the oxides of Si, Fe and Mg. The absence of Na and K would appear to account for the higher average melting point of this second phase relative to that of the CTH whiskers (1300 versus 1100° C).

Although the disintegration of many whiskers resulted from melting of the second phase during anneals at 1000 to 1300° C, a significant percentage of both CTH ($\sim 30\%$) and TFI whiskers ($\sim 50\%$) were not affected by this process. In these whiskers localised surface pitting was noted after an 1000° C anneal, but only became extensive after heat treatment at 1400 to 1500° C in the CTH whiskers. Many of these pits were associated with second phase particles, as has been discussed previously, but it is also necessary to account for the pits in impurity-free regions. The localised distribution and sharply radiused form of the pits observed experimentally do not conform to the periodic convolutions predicted theoretically on a capillary induced surface

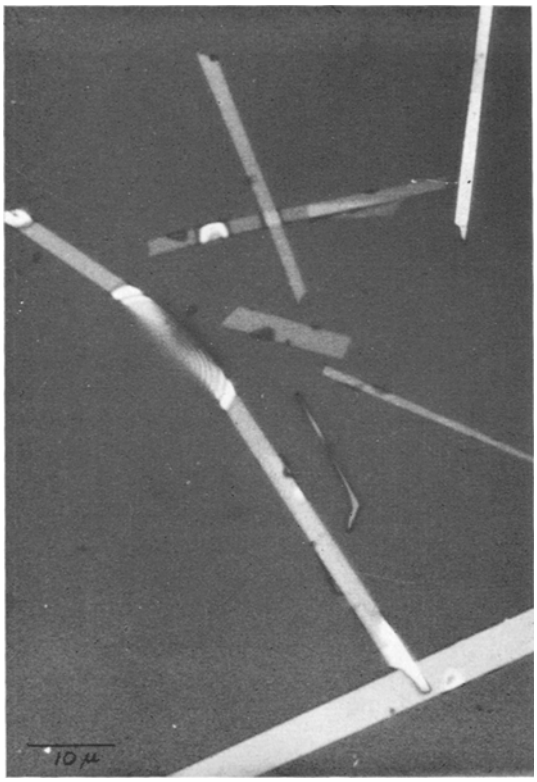


Figure 26 Internal stress distribution (TFI whiskers).

diffusion model [7]. Hence it is unlikely that self-diffusion of Al_2O_3 by itself would produce the surface pits. These results are consistent with the observations of Stapley and Beevers [8] that a treatment at 1400°C for 67 h in vacuum, i.e. longer than used in the present experiments, was required for "waist formation" in sapphire whiskers. Hence it is suggested that these surface pits resulted from diffusion, promoted by local regions of large internal stress. The presence of such stress fields, which would seem probable due to the limited extent of plastic flow possible in sapphire, was experimentally confirmed by observations under polarised light, as shown in fig. 26.

5. Conclusions

(a) Many CTH whiskers (6% silicon) contain "grown in" second phase particles. During anneals in high purity argon above 1000°C particle nucleation, coarsening and coalescence occurs in the larger whiskers, and spheroidisation is produced on the surface of the smaller whiskers.

(b) The activation energy for diffusion of the impurity ion(s) (largely silicon) is approximately 37 kcal/mole. The kinetics of particle coarsening are in general agreement with Wagner's volume diffusion theory.

(c) Surface steps, which are associated with the coarsening of second phase particles, are attributed to the diffusion of the impurity ion(s) at the annealing temperatures.

(d) Melting of the second phase occurs between 1000 and 1400°C, depending on the composition, and produces disintegration of the whiskers.

(e) Some TFI whiskers (0.2% silicon) melt at 1300°C due to the presence of a second phase surface coating.

(f) The whiskers which do not disintegrate due to second phase effects exhibit extensive surface pitting at 1400 to 1500°C, which is attributed to the presence of regions of large internal stress.

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