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(54) Zirconium based alloy.

(57) A Zr based alloy with 7-15% by weight Nb and 0.5-3% by weight Al can be quenched in water from 1000°C to largely retain beta phase. It is then deformable at room temperature to produce martensite.

The alloy, which can be made in an electric arc furnace and forged at 900°C to destroy the original solidification structure, is particularly suitable for structural components and fuel elements of nuclear reactors.

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"ZIRCONIUM BASED ALLOY"

The present invention provides a zirconium base alloy with niobium and aluminium as alloying elements and a method for obtaining the said alloy. The alloy of this invention presents a low content of the niobium and al-
5 uminium alloying elements and provides an alloy which has particular value in the fabrication of structural components and fuel elements of nuclear reactors.

In the field of nuclear reactors it is desirable to make components such as tube cladding, pressure tubes,
10 calandria tubes, tubes for control channels and for measurements inside the reactor, etc. which present a low effective capture cross section for thermal neutrons with no detrimental loss of good mechanical properties.

Up to the present time efforts have been made to
15 get a compromise solution by avoiding the over-dimensioning of components to obtain good mechanical properties, as well as their sub-dimensioning to give a low capture cross section for neutrons. Zirconium is a metal which has low capture cross section for thermal neutrons (0.18 barn)..
20 Due to its good mechanical properties, it is the metal which has the lowest capture cross section for a given mechanical design load.

The resulting thickness of spare parts will absorb less neutrons than if any other metal were used for its
25 fabrication.

Different elements have been used as alloying elements for Zr in order to improve its properties, amongst them Sn, Mo and Nb. However, up to the present time, no material has been obtained which is stable with temperature, and which has sufficiently good mechanical properties, as for example a good ratio between maximum tension and total elongation to fracture and with no difficulties in the fabrication of components.

Alloys obtained up to now have not been sufficiently ductile, thus making difficult the shaping of spare parts by mechanical machining.

Regarding the pseudo-elastic effect, the necessary, though not sufficient condition, for it to occur is the induction of martensitic phase transformation by deformation of the material.

In Zr, the high temperature (bcc) beta phase is stable above 1,133 K (860°C) whereas at lower temperatures one has the (hcp) alpha phase. In the binary Zr-Nb alloy with low Nb components (less than 6.5 weight %) a martensitic phase is obtained after quenching. If the Nb component is between 6.5 weight % and 20 weight %, the beta phase is retained and omega precipitates appear after quenching the sample. If the Nb content is greater than 20 weight % only the beta phase is retained after quenching.

As is well known, this is due to the Zr-Nb phase diagram. The behaviour is explained by the Lucke criteria, according to which, if, in a Ti or Zr (valence 4) alloy, an

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alloying element is added with a large number of electrons or with a valence higher than 4, then the high temperature beta phase is stabilised.

In short, stability is directly related to the number of electrons per atom De/a . For pure Zr De/a is equal to 4.00.

If De/a is equal or less than 4.06, martensite is obtained by quenching. If De/a is equal to or greater than 4.14 only the beta phase is retained. If $4.06 \leq De/a \leq 4.14$, the beta phase with omega precipitates is retained. From the studies which are performed in this field and which are the basis of the present invention, it has been proved that it is very difficult to modify the beta phase of Zr alloys with Nb contents between 7 and 15 weight % by means of thermo-mechanical treatments. The material becomes very brittle, possibly due to the presence of omega, and, when it is attempted to deform it, fracture occurs with no observable phase change.

If the Nb content is greater than 20 weight %, only the beta phase is stable and no new phase can be induced upon deformation. It should be mentioned that Nb has a valency of 5 and is a beta stabiliser.

In search for a solution of the above-mentioned problems, the binary alloys Zr-Nb have been modified by the addition of Al, which having a valency of 3, acts in opposition to Nb and favours the alpha phase stabilisation.

One of the aims of the present invention is to develop a method to obtain a ternary Zr-Nb-Al alloy capable of retaining the high temperature beta phase by quenching, in order subsequently to induce by deformation
5 a martensitic phase in the material.

A second aim of the present invention is to devise a method to obtain a ternary Zr-Nb-Al alloy which by deformation would allow the induction of a martensitic phase (not only deformation by slip) which would make possible
10 the elongation of the material with a high degree of hardening.

It is, also, another aim of the present invention, to provide a ternary alloy which overcomes the drawbacks and shows the advantages above stated.

15 It is, finally, another objective of the present invention, to provide a ternary Zr-Nb-Al alloy which presents ductility, high maximum fracture tension and high elongation, properties which make it especially apt for its application in the fabrication of components of or for
20 nuclear reactors.

These objectives have been realised by modifying the Zr-Nb alloy with the addition of Al, and through the original procedure that will be described further, a new material has been obtained which is ductile and suitable
25 for applications in the field of nuclear metallurgy.

In fact, by adding for instance 1 weight % Al (alpha stabiliser) to the binary alloy Zr-Nb, with Nb

content of say 10 weight %, it was beta phase and a modification of the omega precipitate which was observed after quenching. This resulted in a more ductile material. Material so made was then deformed by rolling at room temperature and at the temperature of liquid air. An evaluation of the phases present was done after each treatment by means of optical and electron transmission microscopy as will be described later.

After deformation of 5% at room temperature, martensite plates are already observed in several grains of the sample, along well defined directions. When rolling at low temperatures to the same amount of deformation, a greater quantity of martensite and a different morphology is observed. While deformation proceeds, for a single cycle of quenching and deformation, the number of martensite plates increases and after 70% deformation some beta phase still remains untransformed.

The invention will be further described by reference to the accompanying drawings in which :-

Fig. 1 shows deformation curves as a function of load for a sample of an alloy according to the invention;

Fig. 2 is a graph showing the critical yield stress as a function of temperature;

Fig. 3 shows the variation of maximum tension and elongation as a function of temperature;

Figs. Nos. 4a, 4b, 5, 6, 7 and 8 reproduce optical micrographs of samples from material according to the invention;

Figs. 9 and 10 reproduce scanning electron microscopy photographs; and

Figs. 11, 12 and 13 are derived from transmission electron microscopy, in each case using samples of an alloy according to the invention with different Nb contents.

The use of Al and Nb as alloying elements for Zr is found convenient because Al also has a low absorption cross section for thermal neutrons (0.23 barns) and that of Nb (1.18 barns) is approximately three times smaller than that for Mo.

By adding the alloying elements in the appropriate ratio to Zr, it is possible to retain the high temperature beta phase (bcc) and afterwards it is possible by deformation to induce in the material a martensitic phase. This behaviour leads to a very interesting mechanical phenomenon known by the name of TRIP (transformation induced plasticity). For the alloy which is the subject of the present invention this mechanical behaviour (TRIP) is observed for a composition range between 7 and 15 weight % Nb and 0.5 to 3 weight % Al.

In order to verify what has been stated above, tension tests were performed using quenched samples with the retained beta phase. The measurements were made at different temperatures between 80 K and 373 K (-193°C to 100°C). In each case the values for the critical yield stress, the maximum and total elongation were obtained.

Thus in Fig. 1 the ordinate is the applied load on the sample versus the percentage of deformation ($\Delta l/l$).100 as abscissa. Fig. 2 shows for the same sample, the critical yield stress as a function of the measured temperature given in the abscissa. Fig. 3 shows two curves, the upper one corresponding the ultimate tensile strength σ_{uts} and the lower one for the corresponding plastic deformation ϵ_f , both as a function of temperature in the abscissa.

From the morphological point of view, the optical micrographs corresponding to Figs. 4, 4a and 4b show the material before the deformation, whereas those of Figs. 5, 6, 7 and 8 refer to the samples after the deformation. The fractured zone with a typical ductile structure was observed by scanning microscopy corresponding to Figs. 9 and 10.

For comparison it may be mentioned that in these alloys but with low Nb content, i.e. below 6 weight %, martensite forms spontaneously on cooling as seen in Fig. 11, a photograph made by transmission electron microscopy. It is noted that its structure is hexagonal close packed with the typical spear-type morphology of martensite. Under these conditions the material has a high elastic strain energy field due to the shape of the martensite. The martensite is internally twinned. On the other hand the material of the present invention is induced by deformation and plates of the following characteristics are found :-

(a) the plates are not internally twinned nor do they exhibit a twin relationship between each other;

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(b) the beta phase matrix appears deformed and contains dislocations, and the induced martensite plates appear accommodated in the matrix.

These characteristics are well visible in electron
5 micrographs corresponding to Figs. 12 and 13. From what has been said and observed it can be concluded that we are dealing with an alloy of a high temperature hysteresis, i.e. the martensite phase induced by deformation is sufficiently stable to heating to temperatures of the order of 600°C
10 (873 K). This indicates the possibility to apply^{the}/alloys at higher temperatures than those commonly used with the known Zr alloys, such as Zircaloy 2 or Zircaloy 4.

The alloy which is obtained in this manner does not have a pseudo-elastic behaviour. For this it would be nec-
15 essary to have a martensitic transformation assisted by stresses, that is to say, that the material would retain the beta phase after quenching and that by applied stresses the martensite would be induced without reaching the normal plastic deformation of the beta phase. In addition, if the
20 pseudo-elastic effect were to exist, the material would recuperate its initial shape after removal of the load.

In this way a material is obtained which exhibits a high fracture stress and considerable elongation, due to the fact that the deformation does not proceed exclusively
25 by slip or twinning (depending on the temperature of deformation), but that during the deformation a new martensitic phase is induced which enables the elongation of the material

with the obtention of a high hardening value.

According to the invention the method for obtaining the above described alloy consists of the following sequential stages :

- 5 (a) in an electric arc furnace, there is melted at least once a Zr base material with an Nb content between 7 and 15% by weight and an Al content between 0.5 and 3% by weight, the amount of oxygen being controlled;
- (b) the alloy thus obtained is forged at a temperature of
10 900°C (1173 K) in order to destroy the original solidification structure;
- (c) after forging the material is quenched in water from 1000 °C (1273 K);
- (d) the material is then deformed at approximately room
15 temperature; and
- (e) Stages (c) and (d) are repeated until an appropriate morphology of the beta phase with the induced martensite is obtained according to requirements.

Control of oxygen in stage (a) is of great importance as it produces solid solution hardening. Typical values
20 by weight are 1000 ppm and 1600 ppm. By the hot forging in stage (b) there is obtained a structure of homogeneous and smaller grains which favours the subsequent mechanical behaviour of the material. After each quenching indicated
25 in stage (c), the beta phase is again retained and the material can be deformed to accomplish the final geometry. During the deformation martensite is induced producing the

so-called TRIP effect. This deformation corresponds to the already mentioned stage (d).

Of course, each deformation cycle is stopped before the fracture stress is reached, and the quench
5 treatment of stage (c) is repeated, which allows the material to be once more deformed. The treatment is ceased when finally a "duplex" is obtained, viz. a beta phase and induced martensite appropriate for the use of the material.

10 Naturally, when practicing the method to obtain the new alloy according to the present invention, changes can be introduced without departing from the scope of the invention.

CLAIMS :

1. A zirconium based alloy having a niobium content of between 7% and 15% by weight and an aluminium content between 0.5% and 3% by weight.

2. An alloy according to claim 1, which, on quenching
5 in water from 1000°C, largely retains beta phase and which is then deformable at room temperature to form martensite.

3. An alloy according to claim 1 or claim 2 having a niobium content of about 10% and an aluminium content of about 1%, both by weight based on the content of zirconium.

10 4. A method of obtaining a zirconium base alloy, comprising the following steps -

(a) melting at least once, zirconium based material with a niobium content of between 7% and 15% by weight, and an aluminium content of between 0.5 and 3% by weight whilst
15 controlling the amount of oxygen present,

(b) forging the obtained alloy to destroy the original solidification structure,

(c) quenching in water,

(d) deforming the material,

20 (e) repetition of steps (c) and (d) as necessary, until an appropriate morphology of the beta phase with the induced martensite is obtained.

5. A method according to claim 4 wherein step (a) is performed in an electric arc furnace, and step (d) is done
25 at approximately room temperature.

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6. A method according to claim 4 or claim 5, wherein step (b) is carried out at at least 900°C and the quenching is effected from at least 1000°C.

7. A method according to claim 4 or claim 5, wherein
5 step (b) is carried out at 900°C and the quenching from 1000°C.

8. A method according to any one of claims 4 to 7, wherein the niobium content is about 10% and the aluminium content is about 1%, both by weight, based on the content
10 of zirconium.

9. A structural component of or for a nuclear reactor made from an alloy according to any one of claims 1 to 3.

10. A structural component of or for a nuclear reactor made from an alloy produced according to any one of claims
15 4 to 8.

FIG.1

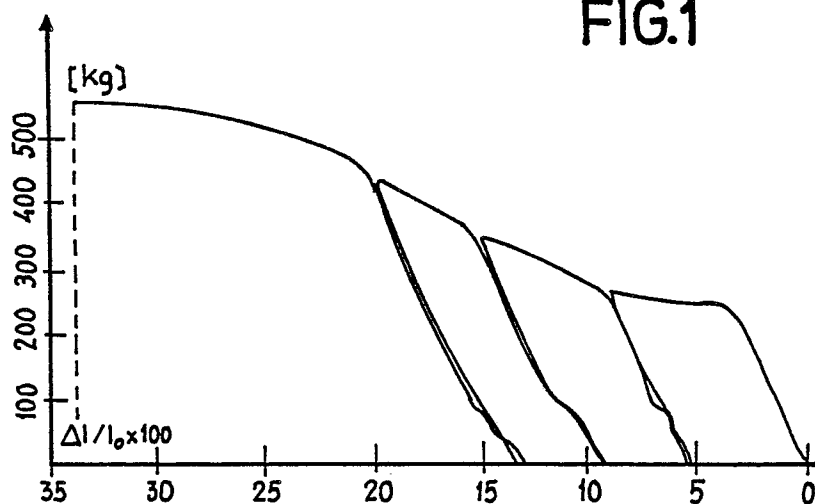


FIG.2

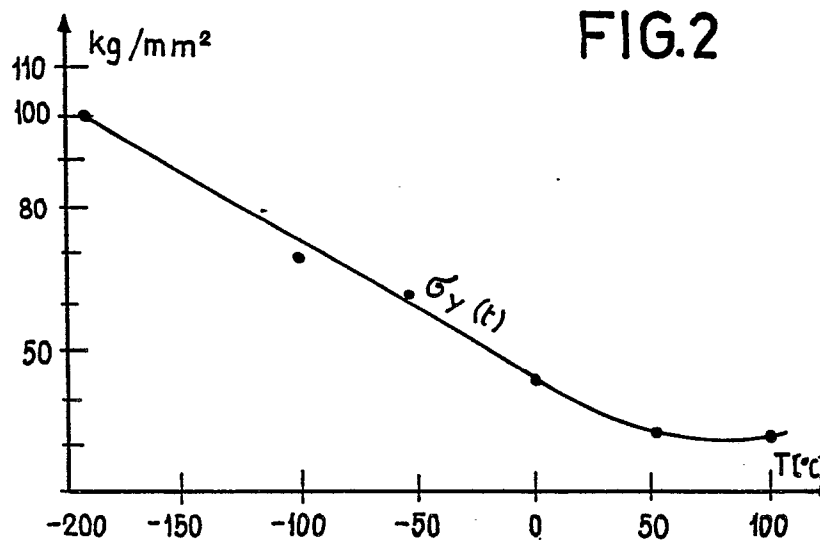


FIG.3

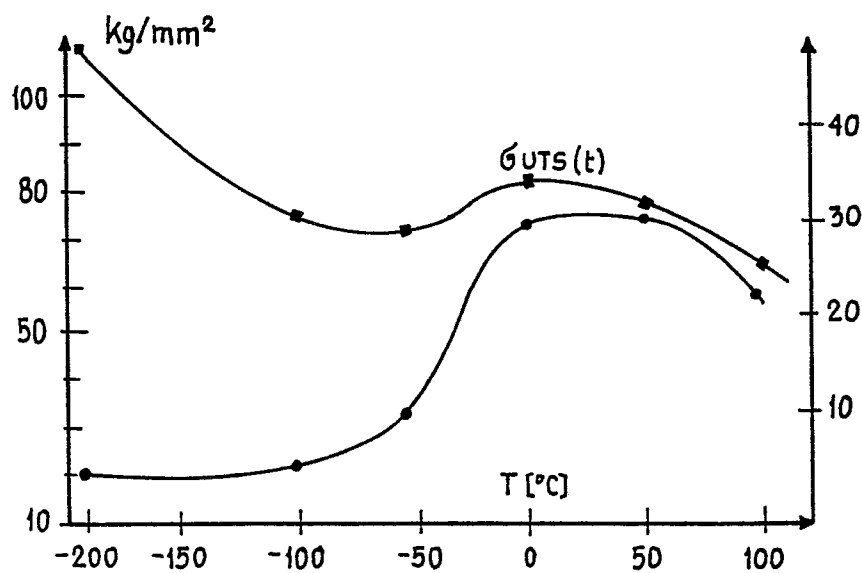




FIG. 4a



FIG. 4b

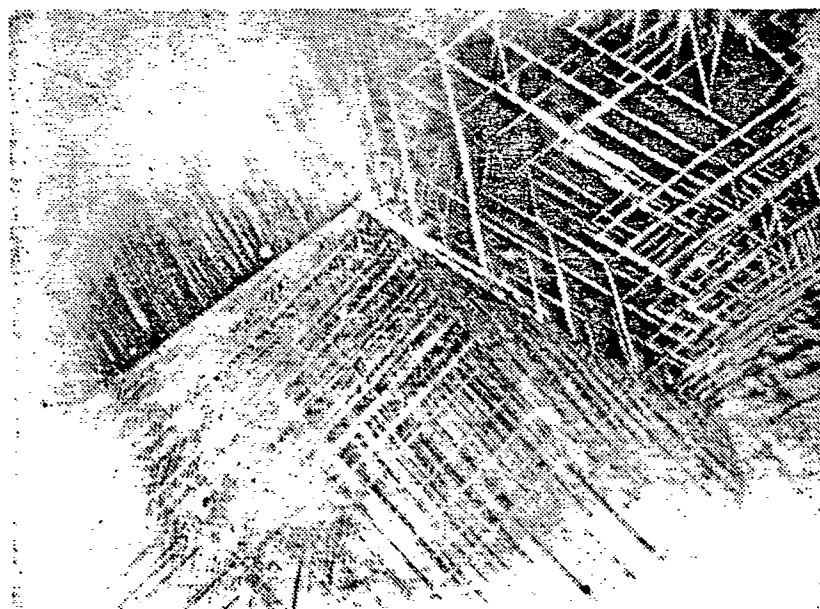


FIG. 5

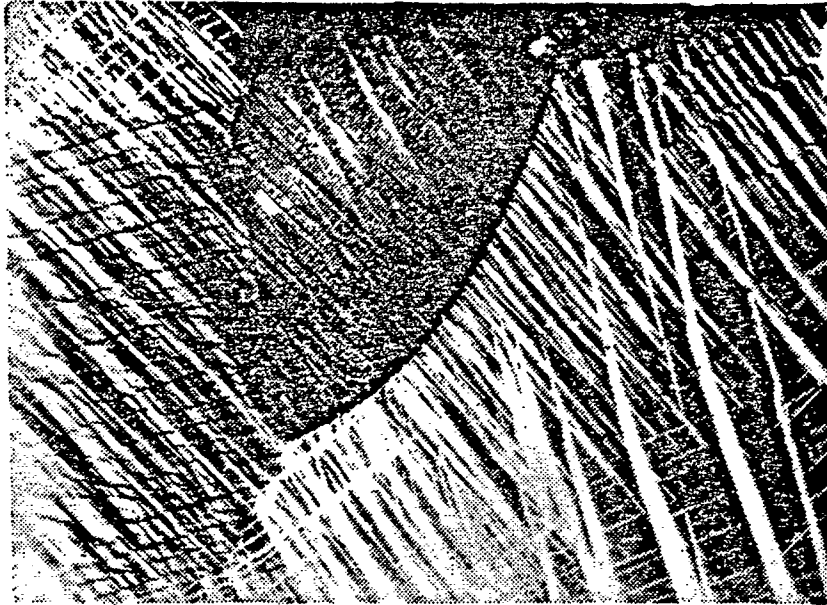


FIG. 6

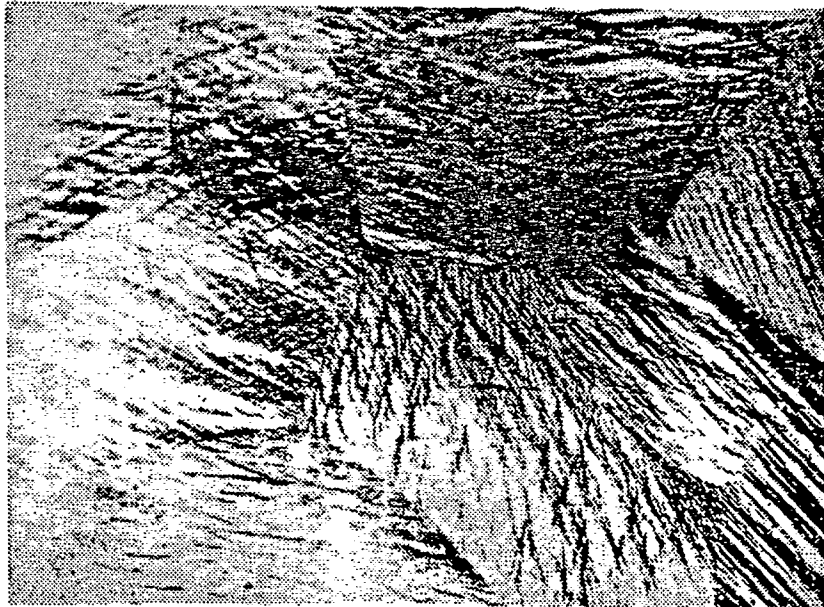


FIG. 7

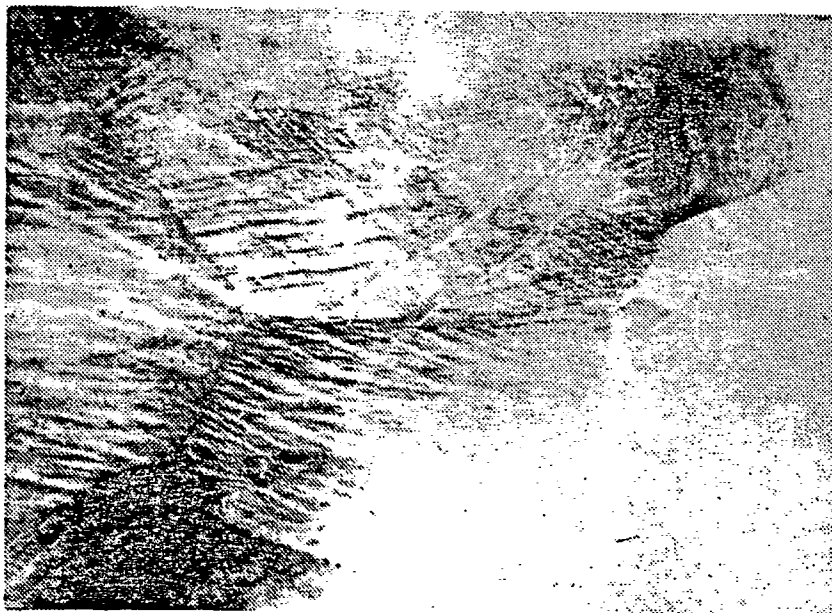


FIG. 8

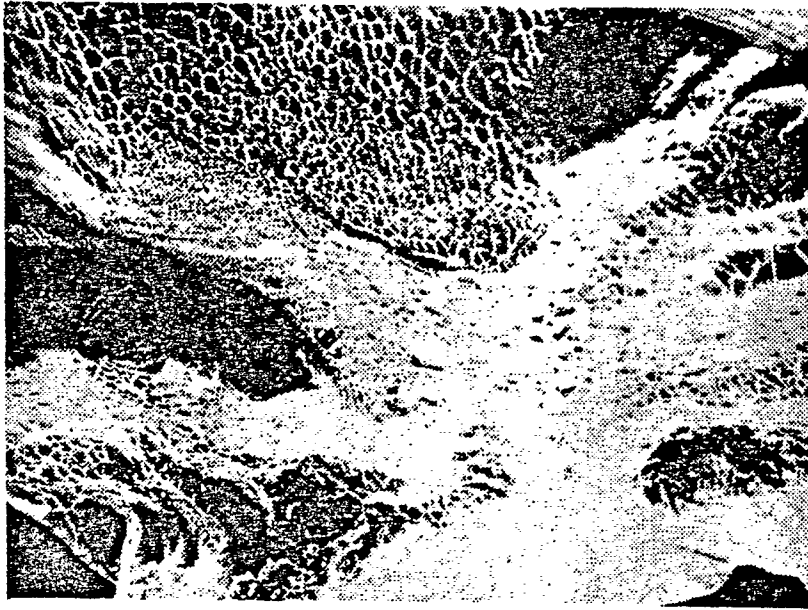


FIG. 9

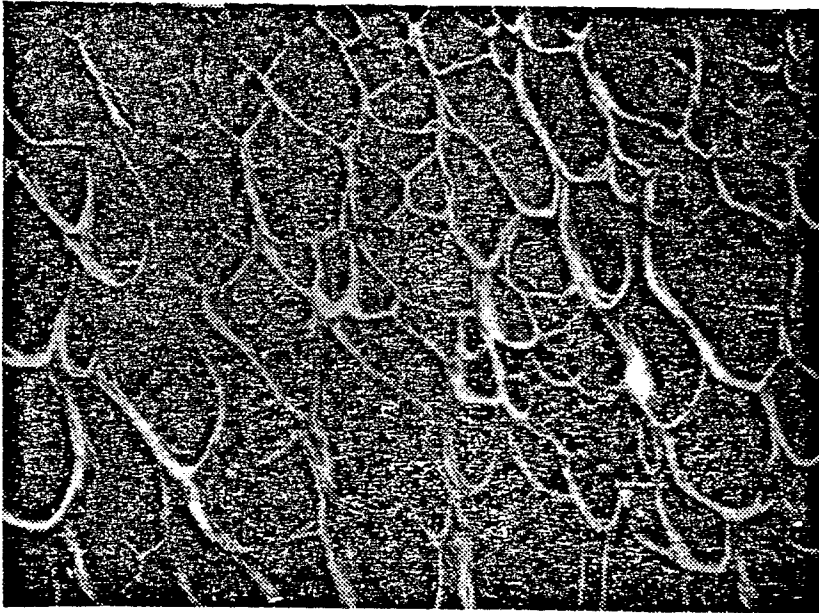


FIG. 10

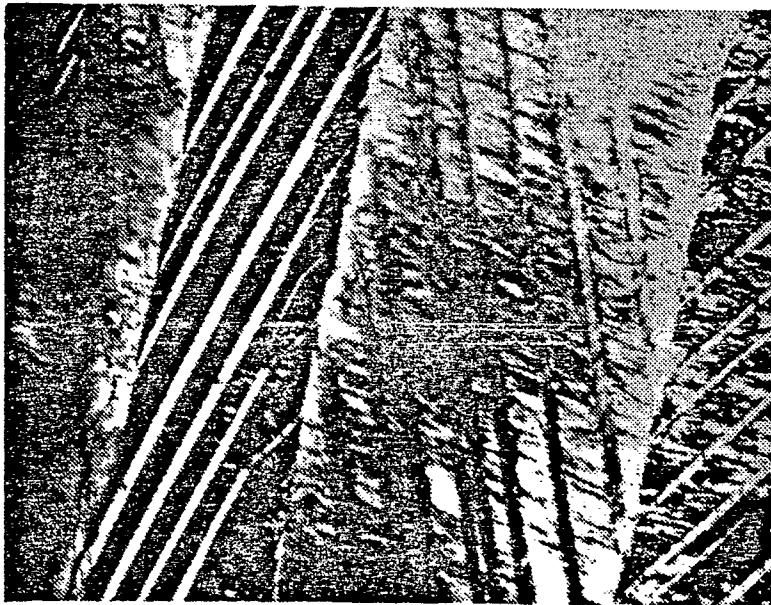


FIG. 11



FIG. 12



FIG. 13