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(54) PROCESS FOR THE SEPARATION OF COMPONENTS IN MULTICOMPONENT MIXTURES, WHEREIN THE DIAGRAM OF BINARY PHASES OF THE TWO MAJOR COMPONENTS PRESENTS A NONOTECTIC AND THEIR DENSITIES ARE DIFFERENT

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No. OF CLAIMS 7

ABSTRACT OF THE DISCLOSURE

A process for the separation of components in multicomponent mixtures, wherein the diagram of binary phases of the two major components presents a monotectic and their densities are different, consisting of successive coolings and heatings of the material to be purified between temperatures above and below the monotectic reaction temperature and/or the solid/liquid transformation temperature, having as a final result the separation of the components in the desired degree, up to the intrinsic limits of the system.

The present invention relates to an industrial process for separation of the two major components in a multi-component mixture, when the two components have in the binary system a monotectic reaction and there are differences between their densities.

The invention will be described particularly with reference to Zn/Pb major component mixtures, but its scope is generic and not limited to such mixtures.

Industrial methods for extraction of metals from their ores yield final products the purity whereof varies according to the process employed and the characteristics of the starting ore. A typical case is that of the difference which exists between the purity of zinc obtained by an electrolytic process as compared with the electrothermic process. In the product resulting from the electrothermic process the typical and major impurity usually is lead, depending on the starting ore.

An industrially used process for decreasing the lead content in electrothermic zinc is described in German patent DBP 1 142 704 and explained in detail in the literature. While this prior art procedure may be effective in decreasing the Pb content, it requires addition of sodium as a third element, and the sodium is not totally eliminated, leaving a residual concentration of about 0.03% in the zinc.

The most frequently used industrial method for purification of electrothermic zinc to remove the lead therefrom utilizes the properties indicated in the liquid-vapor system phase diagram and involves distillation. By means of this process zinc of a purity comparable to the electrolytically-

produced product can be obtained.

The process of the present invention results in an intermediate purity product insofar as removal of lead is concerned and is based on the properties of the solid/liquid equilibrium diagram, as well as on the kinetic type phenomena governing the solid/liquid transformation of the major components binary system; in this particular case, the Zn/Pb system. The advantages of the method of the invention arise from a comparison of latent heats of fusion and vaporization, indicating a considerable decrease in the cost of the process and simplicity of equipment construction, operation and maintenance.

It is well known that differences in composition between phases in equilibrium in multicomponent systems cause segregation phenomena in the course of processes involving more than one phase, particularly the solid/liquid type. While in the case wherein a final product having a uniform composition is required, segregation must be avoided, segregation, conveniently promoted, may be used in separation processes. Typical examples thereof are the fractional distillation processes, widely used in chemistry, of nonmetal solutions and the zonal fusion purification process. Separation can be more effective in cases in which there is a remarkable difference in density between the solid and the liquid and what is desired is simply to obtain a separation of solid-liquid of different compositions. This separation may be intensified by means of centrifuging.

The present invention is directed to a process which, based on the mechanisms governing the alloy solidification process, enables the separation of the two major components in a multicomponent alloy, up to an acceptable limit for certain

industrial uses. For the method of the invention to be effective, it is necessary that the components satisfy the following conditions: (1) that they present a monotectic transformation in the binary system, and (2) that they differ in density. The method will be exemplified for the case of a multicomponent alloy having zinc and lead as major components, with a lead content which may be greater or lesser than in the monotectic composition.

The process of separation of the present invention is based on successive coolings and heatings of the material to be purified, between temperatures above and below the monotectic reaction temperature and/or solid/liquid transformation temperature, having as a final result separation of the components in the desired degree, up to the limits the system will allow for reasons intrinsic thereto. The method has proven to be effective both with hyper- and hypo-monotectic composition materials. Maximum and minimum temperatures, as well as the time during which the material is maintained at the monotectics temperature and/or the solid/liquid transformation temperature, may be varied over wide ranges.

The process is more effective if, as physical separation of the components advances, liquid rich in one of the components is removed, for example, lead in the case of the Zn/Pb system, so that the tendency of the system to homogenize again for thermic reasons, for example diffusion or convection, is minimized.

The following description of the invention makes reference to the accompanying drawings, in which:

Figure 1 is a graphical plot of the quantity of

lead impurity in a zinc ingot against the number of cooling and heating purification cycles;

Figure 2 is an equilibrium phase diagram of a zinc/lead binary system;

Figure 3 is a schematic representation of a sequence of positions of impurities in a molten composition during the purification procedure;

Figures 4a and 4b are photographs of, respectively, the upper and lower part of a zinc/lead specimen treated in accordance with the present invention; and

Figure 5 is a photograph illustrating the movement of impurities through a molten body of zinc/lead.

The process of the invention makes it possible to obtain substantially hypomonotectic compositions starting from both hyper- and hypo-monotectic composition material. The process may be described in more detail as follows: a material the two major components of which are A and B and having an initial composition of X_A and X_B is provided. Starting from an initial temperature $T_1 > T_M$, where T_M is the temperature of the monotectic or of the solid/liquid transformation, the material is cooled at a desired rate of cooling, which may vary over a broad range, and then is maintained at the temperature of the monotectic and/or of the solid/liquid transformation for a variable period of time, which may be sufficient or insufficient as desired to permit the total transformation of the material.

In the event that the material is totally transformed, cooling is continued down to a temperature $T_2 < T_M$, at a desired rate which may vary over a wide range. Temperature T_2 also

may vary over a broad range, but practise has indicated that it is not necessary for temperature T_2 to be much below the temperature of the monotectic or of the solid/liquid transformation.

The prcedure then is repeated in the reverse direction, with the material being heated to temperatures above T_2. The rate of heating may vary as desired over a broad range and once the temperature of the monotectic and/or of the solid/liquid transformation has been reached, the material is maintained at that temperature for a desired period of time, which may be sufficient or insufficient as desired to permit total transformation, and then, if permitted, the temperature of the material is raised at a desired rate which may vary over a broad range up to a temperature T_1', which may be higher, the same as or lower than the initial temperature T_1, and the maximum temperatures of the successive heatings to which reference will be made hereinafter. By repeating the above procedure as many times as necessary and always maintaining variable or not the maximum and minimum temperatures, the heating and cooling rates, as well as the time for which the material is kept at the monotectic and/or solid/liquid transformation temperature, considerable purification of the initial material may be achieved.

The process of the invention as outlined above has been shown to be effective both with ingots below 1kg (that is on a laboratory scale) as well as with an industrial type ingot. The criterion for selecting a given maximum and minimum temperature, a given rate of heating and cooling, as well as a given time of residence at the monotectic and/or solid/liquid

transformation temperature, in each cycle, is to favor the mechanism of separation which, in each stage of the process, is considered to be the most effective, or convenient.

The procedures are carried out with any convenient method of heat removal and supply, using known apparatus such as salt-bath furnaces, radiation furnaces and, in general, any means capable of providing the necessary amount of heat to carry out the above operation, irrespective of the source of energy.

The process of the invention contemplates removal of material rich in the heavier component from the lower part of the mold, such as, through a high temperature valve or a port allowing metered, discontinuous or continuous, exit of the material, in the liquid state during the whole separation method. Removal of the purified material then may take place from the upper part of the mold in the liquid state, utilizing any convenient system of elevation of the material, for example, vacuum, a suction pump, or by simply tilting the mold.

In the specific case of the Zn/Pb system, the final product consists in a lead-rich material in the lower part of the ingot, while the remainder is zinc of a purity higher than the starting material. This may be clearly seen in the photographs of Figures 4a and 4b of a specimen which was submitted to a treatment as described above.

Figure 4a shows the upper part and Figure 4b the lower part of the specimen. It may be clearly seen that in the upper region there is a lesser quantity of lead-rich particles than in the lower region. In the periphery of the lower part, cavities may be seen which were occupied by the

lead-rich phase, which settled, and was removed therefrom during the metallographic treatment the specimen was given.

A typical example of operative values utilizable in the above described method of the present invention is T_1: about 430°C, T_2: about 400°C; total time of one heating and cooling cycle: about 14 minutes, with a residence time at the temperature of the monotectic of about 6 minutes, both in the heating and in the cooling phases of the cycle; after several cycles and starting from zinc having a lead content above 1.4% by weight, a material was obtained having a purity such that the lead percentage was below 0.04% by weight.

The importance of removing the denser material during the purification method is shown by the curves in Fig.1, which represents the lead percentage, by weight, in a zone of the ingot in question as a function of the number of cycles, for the example under consideration. The upper, solid line, curve represents the case in which no material removal is made, while the lower, dotted line, curve represents the case wherein when the material reaches a certain concentration (0.20% lead by weight in the case illustrated), a removal of material is made from the lower zone of the ingot which is less than 10% of the ingot total, then the thermal cycling of the material is continued. It may be seen that the same final concentration of 0.04% lead by weight is obtained in approximately 140 cycles in the event that no removal of material is made, while 98 cycles are needed in the case but one removal alone of material is carried out. In both cases the average initial concentration of Pb in the ingot was above 1.2% by weight and was approximately 1.4%.

The importance of conducting a removal of material very rich in the denser element is observed in the final concentration obtained for a same number of final cycles. For the thermal treatment conditions under consideration, if the material is subjected to 23 cycles of heating and cooling a purity of 0.28% lead by weight in a certain zone of the ingot is obtained. If on the other hand the same number of cycles is applied in the following way: 10 cycles, then a removal of material is effected by the lower part of the ingot, of the order of about 10% of the total ingot, and then a further 13 cycles similar to the first ones is applied, a purity of 0.082% lead by weight is obtained.

A number of mechanisms operate in the separation of the elements, in the process of the present application. For the better understanding thereof reference is made to the phase diagram of Fig.2, wherein is shown the diagram of equilibrium phases typical to a binary system presenting a monotectic reaction. It shall be assumed that element B is denser than element A and, in the specific embodiment applied to the system Zn/Pb, it shall be understood that element A represents zinc and element B represents lead.

If a liquid mixture of a composition higher than the monotectic, for example, C_E in Fig.2, is obtained through a given extraction process, from observation of the equilibrium diagram it shall be seen that a first separation may be obtained if the liquid mixture is maintained for a period of time at temperatures such that liquids L_1 and L_2 coexist. As these two liquids differ in density, settling of the denser one occurs. This is the method used industrially to purify

the zinc obtained by electrothermal processes starting from a zinc-rich material having a high lead content, a partial separation of both components being produced. It will be seen from Fig.2 that this prior art process of separation has a limit established by the composition of the monotectic, that is, a material having a B content lower than C_M cannot be obtained. Thus, in the case of the Zn/Pb system, the monotectic composition of which is 0.9% lead by weight, zinc is obtained with a lead content by weight within the range of 1.2 and 1.4%, a value that may be considered very good for an industrial process of that type.

As indicated earlier, the method of the present invention makes it possible to purify the basic material down to B (lead) contents far below the monotectic composition. The mechanisms of separation of components may be divided into a number of sub-headings.

I) Gravity separation in heterogeneous liquid phase

This is the mechanism indicated above for obtaining material close to the monotectic composition. Of course, it will only be effective for compositions above the monotectic and will operate for all the ingot during the first cooling, but will become less efficient in successive cycles, as the portion of ingot having a concentration above the monotectic decreases.

II) Gravity separation in homogeneous liquid phase

When the starting composition is close to the monotectic, by maintaining the material at a temperature such that it will be in a monophasic

liquid state, that is, homogeneous such as in the L_1 zone in Fig.2, due to the difference in density of the substances forming the mixture, and as foreseen by thermodynamics, a concentration gradient is produced owing to the difference in density between components A and B of the liquid phase. This mechanism however renders a continuous distribution of B in A, with a not very high concentration gradient.

III) Settling of L_2 generated by monotectic transformation during solidification.

Upon solidifying the liquid having a composition close to the monotectic, during liquid-solid transformation, α , L_1 and L_2 coexist (see Fig.2). The liquid L_2, product of the monotectic reaction, may partly be trapped by the solid, but may also partly settle within L_1. Falling spherules of L_2 can be united and coalesce therebetween forming larger spherules, which will result in a more effective separation, since according to Stokes' law they will fall at a higher limit of velocity.

IV) Formation and falling of L_2 in the solidification front.

When the material contains an amount of element B below the one corresponding to the monotectic composition, and if $k_o < 1$, where k_o is the solute partition coefficient, rejection of the solute by the solid may originate an increase in the concentration of liquid in front of the solid/liquid

interphase. This increase in composition may be of such a magnitude that in that zone the liquid reaches the monotectic composition, and mechanism III then operates.

In the event that the increase in concentration is not sufficient for the liquid to acquire the monotectic composition in front of the interphase, in this event there will be L_1 liquid richer in element B, and convective currents of constitutional origin will be originated which will carry the denser liquid towards the lower zones in the ingot.

V) Refloating of phase α.

In the liquid/solid transformation generally the solid is denser than the liquid. But when dealing with alloys components whereof differ in density, it may happen that the solute content will increase the density of the liquid above the density of the solid, thus producing refloating of the latter. When this occurs in monotectic transformations, refloating of α, as well as settling of L_2, is produced, thus increasing efficiency of the separation.

On the other hand, when the material is situated in the field $\alpha + L_2$, if phase L_2 is continuous refloating of α may occur. It should be noted that this mechanism works both in the solidification and the melting of the material, as phase α is the one having the higher melting temperature.

For this mechanism to work it is necessary that the solid is free in the liquid, as when nucleation thereof occures within the liquid. When the solid nucleates on the walls of the mold, and grows inwardly in a direction opposite to the heat extraction direction, multiplying mechanisms may operate which break up existing crystals, placing them in condition for refloating. This mechanism has in some aspects a certain relation with the one described by Allen and Isserow, where separation of U/A type eutectics is promoted, a procedure different from that of the present invention, which refers to monotectics. For the eutectic, however, its working is dubious as the solid phases do not nucleate and grow independently.

VI) Falling of spherules of L_2 during melting.

In the part of the cycle in which melting of the material is produced, the first to melt are the zones which originated in the L_2 spherules formed during the preceding part of the cycle and were trapped in the solid α. These zones of L_2 liquid then begin to react with the surrounding material, consisting principally in phase α, so that zones are formed where L_1 and L_2 coexist, the falling of L being produced while it is reacting with phase α.

This is shown schematically in Fig.3.

This mechanism operates until phase L_2 is completely dissolved, and for this reason it will be more effective the larger the L_2 spherules are. The photograph of Figure 5 is a photomicrograph showing the working of this mechanism in a specimen of Zn/Pb which was tempered in water during the melting in the sixth cycle.

In order that the mechanisms operate with a maximum efficiency, the total cycle times, maximum and minimum temperatures heating and cooling rates, and proportion of transformation in the melting and solidification are chosen for maximum effect, which may be different between one and another cycle.

Modifications are possible with the scope of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the separation of components in multi-component mixtures, for the case where the diagram of binary phases of the two major components to be separated presents a monotectic and their densities are different, which comprises the steps of (a) melting the mixture and heating it to a first maximum temperature above the temperature of the monotectic and/or of the solid/liquid transformation depending on the composition of the mixture; (b) cooling the mixture from the maximum temperature, controlling the rate of cooling until a temperature about that of the temperature of the monotectic transformation is reached; (c) maintaining the mixture at the temperature of the monotectic transformation for a pre-established period of time; (d) cooling the mixture at a controlled rate down to a temperature below the temperature of the monotectic transformation; (e) heating the material at a controlled rate from the lower temperature reached up to the temperature of the monotectic transformation; (f) maintaining the mixture at the temperature of the monotectic transformation for a pre-established period of time; (g) heating the mixture at a controlled rate to a second maximum temperature above the temperature of the monotectic and/or of the solid/liquid transformation depending on the composition of the mixture, wherein the second maximum temperature may be higher, the same or lower than the first maximum temperature; and (h) separating from said mixture liquid rich in said denser component.

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2. The process of claim 1 wherein the sequence of steps (a) to (g) is cyclically repeated as many times as necessary to obtain a determined degree of separation of the components.

3. The process of claim 1 further comprising removing the denser component continuously or discontinuously during the course of the process.

4. A process for separating lead from a multi-component zinc mixture comprising the steps of:

(a) melting and heating the mixture to a temperature of at least 420°C;

(b) cooling the mixture from the maximum temperature, while controlling the rate of cooling, until the temperature at which monotectic reaction occurs is reached;

(c) maintaining the mixture at a temperature between about 417°C and 320°C for a period of time of at least 6 minutes;

(d) cooling the mixture to below the temperature of the monotectic at a controlled rate;

(e) heating the mixture from the lower temperature reached up to the monotectic at a controlled rate;

(f) maintaining the mixture at the monotectic temperature for a pre-established period of time;

(g) heating the mixture to a higher temperature from that of the monotectic and/or the solid/liquid transformation;

(h) repeating the process cyclically as many times as necessary to obtain determined degree of separation of the components into a zone rich in Pb and a zone rich in Zn;

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(i) removing the denser component continuously or discontinuously at any time during the course of the process; and

(j) separating the zone rich in Pb from said mixture.

5. A process for separating lead from a multi-component zinc mixture, wherein Zn and Pb are the major components of said mixture, with compositions of Pb above or below the composition of the monotectic of the Zn/Pb system and assuring a physical separation of zones of material with any composition of Pb between the starting composition and compositions below 0.04% in Pb in Zn and those having more than 90% Pb in Zn, said process comprising the steps of:

(a) melting and heating the mixture to a temperature above the temperature of the monotectic and/or the solid/liquid transformation temperature, depending on the mixture;

(b) cooling the mixture from the maximum temperature, while controlling the rate of cooling, until the temperature at which monotectic reaction occurs is reached;

(c) maintaining the mixture at that temperature for a pre-established period of time;

(d) cooling the mixture to below the temperature of the monotectic at a controlled rate;

(e) heating the mixture from the lower temperature reached up to the monotectic at a controlled rate;

(f) maintaining the mixture at the monotectic

temperature for a pre-established period of time;

(g) heating the mixture to a higher temperature from that of the monotectic and/or the solid/liquid transformation temperature, according to the composition of the mixture under treatment to form a zone rich in Pb and a zone rich in Zn; and

(h) separating the zone rich in Pb from said mixture.

6. The process of claim 5, wherein the temperature of step (a) is at least 420°C, the period of time in steps (c) and (f) is at least 6 minutes, and the temperature of step (c) is between approximately 417°C and 320°C.

7. The process of claim 5, wherein the process is cyclically repeated as many times as necessary to obtain a determined degree of separation of components.

A

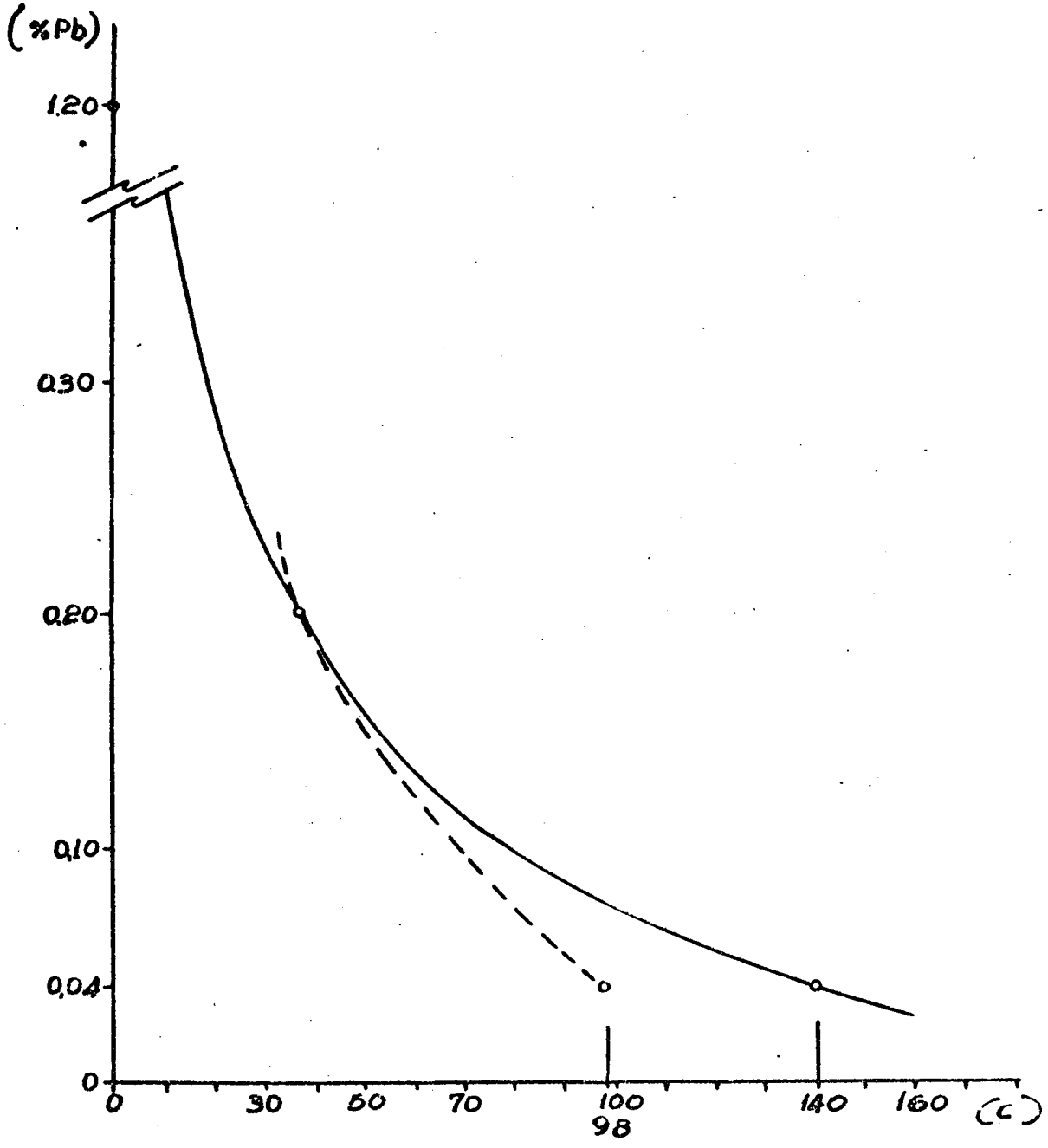

FIG. 1

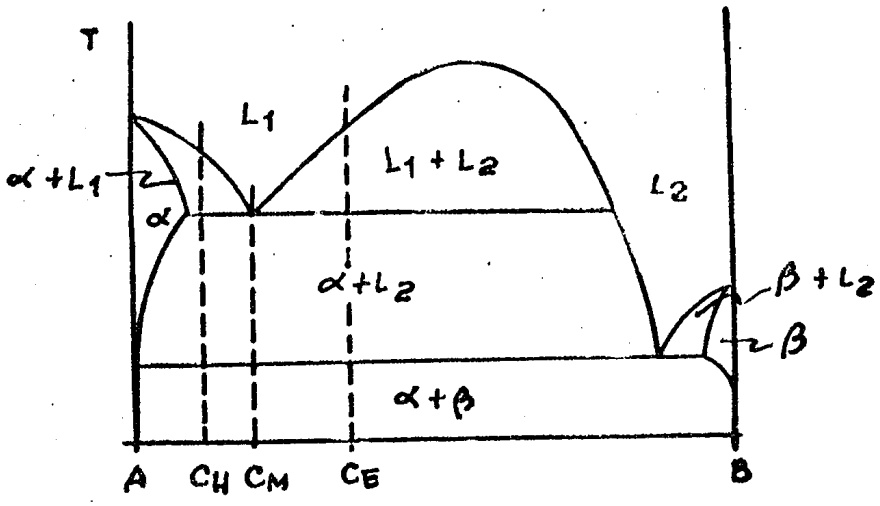

FIG. 2

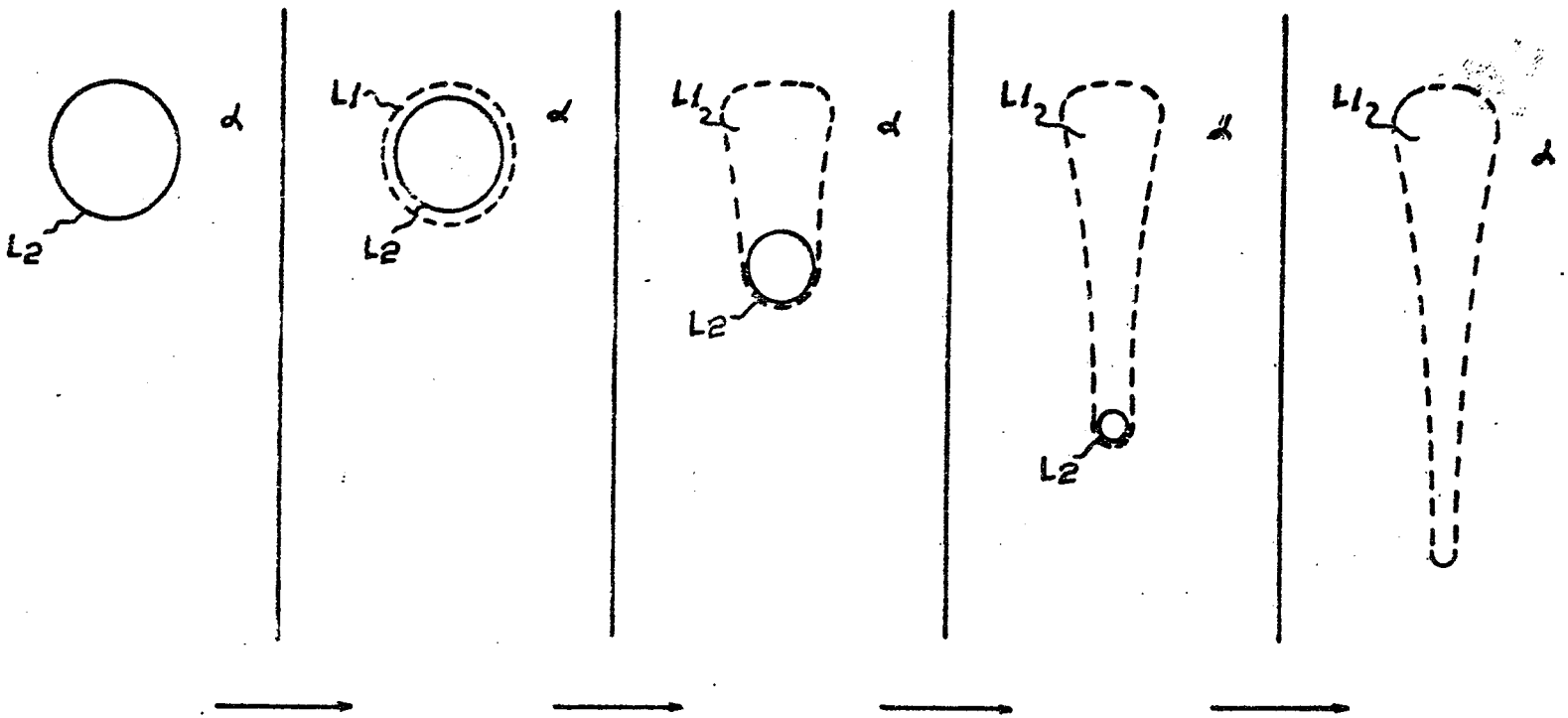

FIG. 3

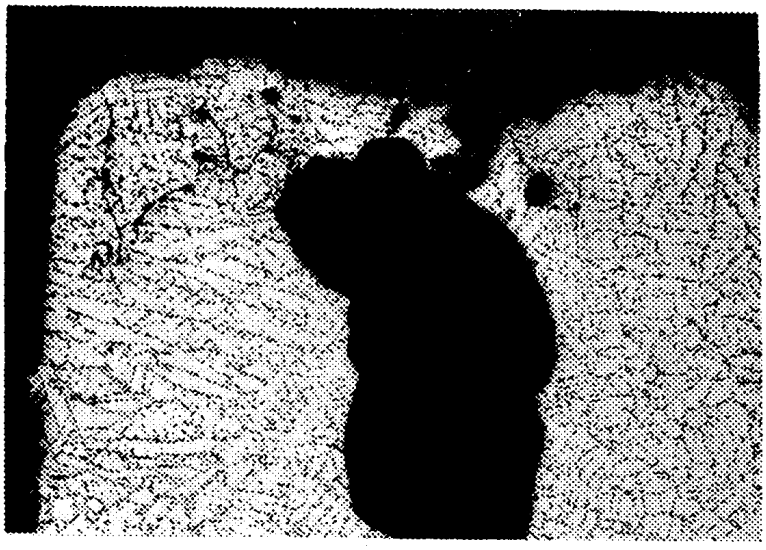

FIG. 4A

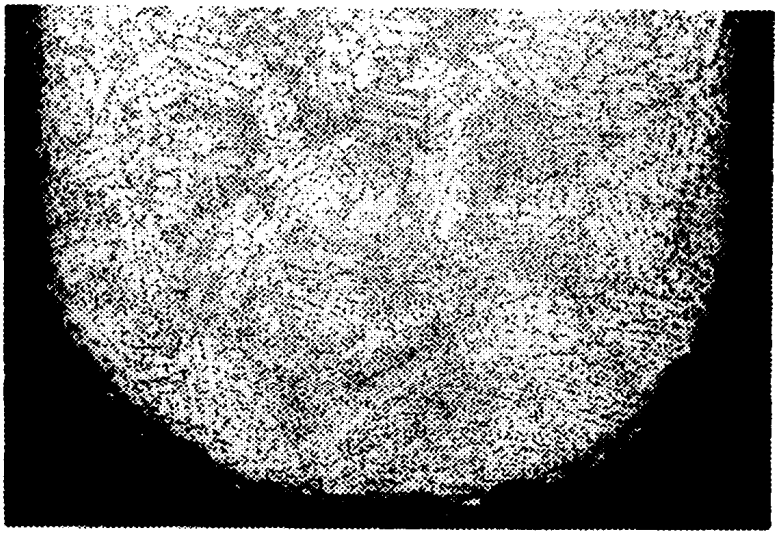

FIG. 4B

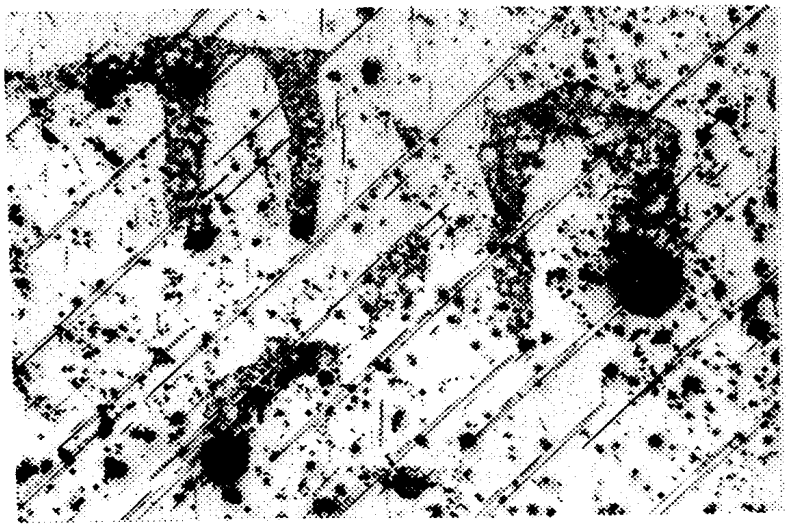

FIG. 5